KINETICS OF MICELLES CATALYZED REACTIONS

ABSTRACT

THESIS

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FARHAT HASAN KHAN

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
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ABSTRACT

The oxidative decarboxylation of amino acids has been subject of interest for several research groups due to its implications in biological systems. A number of inorganic and organic oxidants have been used to investigate the kinetics of these reactions. Hogg and Krishna[1] studied the kinetics of oxidative decarboxylation of glycine, DL-alanine and valine and by N-bromosuccinimide (NBS) and proposed three alternative routes for the decarboxylation of amino acids. Hiremath[2] et al. investigated kinetics of oxidation of some amino acids by 1-chlorobenzotriazole (CBT) in perchloric acid medium and compared the results obtained with chlorine water and HOCl as oxidant. The authors proposed a mechanism consistent with the oberved kinetics. Ramachandran and Co-worker[3-5] carried out a detailed investigation on the kinetics of oxidation of amino acids by different oxidatns like peroxomono sulfate (PMS), N-chlorosuccinimids (NClS) and N-bromosuccinimids (NBS) and chloramine-T (CAT). Gowda and Co-workers[6-10] used chloramine-T (CAT), Bromamine-T (BAT) and dichloramine-T (DCT) for the mechanistic studies of decarboxylation of amino acids.

In view of great similarity with the enzyme catalyzed reactions[11-14], the surfactant catalyzed reactions have

attracted interest of number of researchers. The similarities of the two reactions are based on (a) both have similar structure containing hydrophobic core and polar group (b) both bind the reacting substrate through non-covalent bond and (c) the rate constant of micelles catalyzed reactions follow sigimoid shaped curve. The catalytic effect of micelles has been attributed to the fact that micelles bring the reacting molecule in close proximity (generally in the stern layer). On the other hand the inhibition may be observed due to adsorption of one reactant and repelling the other by the polar micellar surface. However, the role of milcelles in the oxidative decarboxylation of biomolescules has been studied in very limited cases. The kinetics of oxidative decarboxylation of amino acids by acid permanganate was studied by Hussain and Ahmad[15-20] both in the absence and presence of sodium dodecyl sulfate (SDS). However, chloramine-T which can be used under physiological condition to bring about decarboxylation of amino acids has been not fully investigated in the presence of anionic and cationic surfactants. The work in this thesis was carried out in order to make a comprative study of the impact of anionic and cationic surfactants on the kinetic parameters and mechanism of decarboxylation of glycine and alanine.

The work in the thesis comparises general introuduction, experimental, measurement and rate constants, results and discussion and comparative study of activation parameters.

Under the topic "General introduction" a survey of literatures regarding the oxidation of amino acids by different organic and inorganic oxidants has been presented. The dependence of the rate of reaction on different parameters and the proposed mechanism have also been given. The structure, role and application of micelles have also been elaborated.

The experimental part of thesis includes the conditions under which the oxidation of amino acids has been investigated, the product were analyzed and the stiochiometry of the reaction was determined. The oxidation of glycine and DL-alanine by chloramine-T yielded amine, aldehyde, ammonia and carbondioxide. The products were identified by their characteristic usual tests. Stoichiometry of the reactions showed that one mole of each amino acids, glycine and alanine, consumed one mole of CAT as reported by Gowda and Lakshimi Rao[21].

$$R'CH(NH_2)COOH + RNCl^-Na^+ + H_2O \longrightarrow R'CHO + CO_2 + RNH_2 + NH_3 + Na^+ + Cl^-$$

Kinetics experiments were performed under pseudo-first order condition employing 10-fold (or greater) excess of amino acid over CAT. Duplicate kinetic runs showed that the rates were reproducible to within ± 5%. During the kinetic runs the required amount of SDS was added as solid directly to the flask containing amino acid solution while for the study of the effect of CPC the appropriate amount of CPC solution was used.

Under the varying conditions of concerntration of amino acids surfactants and hydrogen ion and temperatures. The kinetics runs were carried out and the results are summarized in tables 1-20 :

Table-1 : Variation of rate constant with glycine concentration at different temperatures in the absence of any surfactant.

Temp.(°C)	30	35	40
[Gly]/M	$^{01}k_{obs}$ x $10^4/s^{-1}$	$^{01}k_{obs}$ x $10^4/s^{-1}$	$^{01}k_{obs}$ x $10^4/s^{-1}$
0.03	2.68	4.22	6.91
0.04	3.07	4.99	8.44
0.06	5.18	7.68	11.51
0.08	6.52	11.13	17.27
0.10	8.44	13.42	22.39
0.12	9.59	15.35	24.95

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3},

[Surfactants] = Nil

Table-2 : Variation of rate constant with $[H^+]$ at different temperatures in the absence of any surfactant.

Temp. (°C)	30	35	40
$[H^+]$/M	$^{01}k_{obs} \times 10^4/s^{-1}$	$^{01}k_{obs} \times 10^4/s^{-1}$	$^{01}k_{obs} \times 10^4/s^{-1}$
0.20	1.14	2.69	4.60
0.15	1.66	2.89	4.99
0.10	1.92	3.26	5.76
0.07	2.30	3.84	6.39
0.06	2.49	4.03	6.65
0.05	2.68	4.22	6.91
0.04	3.07	4.99	8.18
0.03	4.03	-	9.21
0.02	5.18	-	12.28
0.01	8.83	-	-

[Gly] = 0.03 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3},

[Surfactants] = Nil

Table-3 : Variation of rate constant with glycine concentration at different temperatures in the presence of SDS.

Temp.(°C)	30	35	40
[Gly]/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.03	1.79	2.81	5.12
0.04	2.30	3.67	5.88
0.06	3.45	5.76	8.44
0.08	4.79	8.06	11.89
0.10	6.14	10.36	15.99
0.12	7.29	12.47	18.55

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

Table-4 : Variation of rate constant with glycine concentration at different temperatures in the presence of SDS.

Temp.(°C)	30	35	40
[Gly]/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.03	1.53	2.69	4.09
0.04	2.05	3.26	5.15
0.06	2.93	4.60	6.65
0.08	4.22	6.52	9.95
0.10	5.37	8.83	12.79
0.12	6.91	10.36	15.37

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [SDS] = 0.02 mol dm^{-3}.

Table-5 : Variation of rate constant with glycine concentration at different temperatures in the presence of SDS.

Temp.(°C)	30	35	40
[Gly]/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.03	1.34	2.30	3.60
0.04	1.79	2.88	4.22
0.06	2.43	4.03	5.56
0.08	3.65	5.37	8.44
0.10	4.60	7.68	10.75
0.12	5.76	8.83	12.79

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [SDS] = 0.03 mol dm^{-3}.

Table-6 : Variation of rate constant with $[H^+]$ at different temperatures in the presence of SDS.

Temp.(°C)	30	35	40
$[H^+]$/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.05	1.79	2.81	5.12
0.04	1.92	3.07	5.37
0.03	2.43	3.64	6.65
0.02	3.84	5.18	8.18
0.01	7.67	10.36	-

[Gly] = 0.03 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}.

Table-7 : Variation of rate constant with glycine concentration at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
[Gly]/M	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$
0.03	2.94	4.03	6.65
0.04	3.71	5.37	8.70
0.06	5.12	8.83	13.05
0.08	7.29	11.89	17.91
0.10	8.82	15.35	23.03
0.12	10.36	17.27	26.87

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [CPC] = 0.002 mol dm^{-3}.

Table-8 : Variation of rate constant with glycine concentration at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
[Gly]/M	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$
0.03	3.45	5.75	8.44
0.04	4.48	7.67	12.28
0.06	6.91	11.89	17.91
0.08	9.59	16.31	23.03
0.10	12.66	22.07	30.70
0.12	15.33	23.99	34.50

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [CPC] = 0.004 mol dm^{-3}.

Table-9 : Variation of rate constant with glycine concentration at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
[Gly]/M	$^{+1}k_{obs}$ x $10^4/s^{-1}$	$^{+1}k_{obs}$ x $10^4/s^{-1}$	$^{+1}k_{obs}$ x $10^4/s^{-1}$
0.03	4.79	7.67	12.28
0.04	6.65	13.05	20.47
0.06	11.89	22.07	35.82
0.08	16.63	29.43	40.94
0.10	23.03	35.50	55.65
0.12	26.87	44.14	63.33

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [CPC] = 0.006 mol dm^{-3}.

Table-10 : Variation of rate constant with $[H^+]$ at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
$[H^+]$/M	$^{+1}k_{obs}$ x $10^4/s^{-1}$	$^{+1}k_{obs}$ x $10^4/s^{-1}$	$^{+1}k_{obs}$ x $10^4/s^{-1}$
0.20	2.30	3.45	-
0.15	-	4.03	-
0.10	2.68	-	-
0.07	-	-	6.91
0.06	3.07	4.98	7.67
0.05	3.45	5.75	8.44
0.04	3.84	6.91	8.33
0.03	4.61	8.44	11.13
0.02	-	11.51	16.31

[Gly] = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3}, $[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.20 mol dm^{-3}, [CPC] = 0.004 mol dm^{-3}.

Table-11: Variation of rate constant with DL-alanine concentration at different temperatures in the absence of any surfactant.

Temp. (°C)	30	35	40
[Ala]/M	$^{01}k_{obs} \times 10^4/s^{-1}$	$^{01}k_{obs} \times 10^4/s^{-1}$	$^{01}k_{obs} \times 10^4/s^{-1}$
0.02	4.99	7.29	10.74
0.05	7.29	11.51	16.12
0.10	17.27	24.56	34.54
0.15	25.71	36.08	47.99

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},

[surfactants] = Nil

Table-12 : Variation of rate constant with $[H^+]$ at different temperatures in the absence of any surfactant.

Temp. (°C)	30	35	40
$[H^+]$/M	$^{01}k_{obs} \times 10^4/s^{-1}$	$^{01}k_{obs} \times 10^4/s^{-1}$	$^{01}k_{obs} \times 10^4/s^{-1}$
0.15	10.74	17.65	24.56
0.10	16.12	23.79	35.31
0.075	19.19	28.40	39.15
0.05	25.71	36.08	47.59

[Ala] = 0.15 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, u = 0.15 mol dm^{-3},

[surfactants] = Nil

Table-13: Variation of rate constant with DL-alanine concentration at different temperatures in the presence of SDS.

Temp. (°C)	30	35	40
[Ala]/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.02	3.45	5.37	7.29
0.05	5.37	8.06	12.28
0.10	13.05	19.19	26.10
0.15	19.19	27.63	39.15

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},

[SDS] = 0.01 mol dm^{-3}

Table-14: Variation of rate constant with DL-alanine concentration at different temperatures in the presence of SDS.

Temp. (°C)	30	35	40
[Ala]/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.02	2.68	3.83	5.75
0.05	4.61	6.14	8.44
0.10	11.51	14.58	21.49
0.15	16.50	20.73	26.83

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},

[SDS] = 0.02 mol dm^{-3}

Table-15: Variation of rate constant with DL-alanine concentration at different temperatures in the presence of SDS.

Temp. (°C)	30	35	40
[Ala]/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.02	2.11	3.07	4.99
0.05	3.64	4.99	6.91
0.10	9.59	12.66	19.91
0.15	13.83	19.96	25.33

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},
$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},
[SDS] = 0.03 mol dm^{-3}

Table-16 : Variation of rate constant with $[H^+]$ at different temperatures in the presence of SDS.

Temp. (°C)	30	35	40
$[H^+]$/M	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$	$^{-1}k_{obs} \times 10^4/s^{-1}$
0.15	8.44	13.82	21.47
0.10	12.28	17.65	27.63
0.075	14.58	20.72	33.01
0.05	19.19	27.63	39.15

[Ala] = 0.15 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},
$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},
[SDS] = 0.01 mol dm^{-3}

Table-17: Variation of rate constant with DL-alanine concentration at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
[Ala]/M	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$
0.02	6.52	10.36	14.39
0.05	12.28	14.39	24.95
0.10	22.07	30.71	44.06
0.15	32.62	42.22	57.57

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},

[CPC] = 0.002 mol dm^{-3}

Table-18: Variation of rate constant with DL-alanine concentration at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
[Ala]/M	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$
0.02	8.44	13.43	17.27
0.05	16.31	19.19	24.95
0.10	28.78	38.38	49.89
0.15	36.46	49.89	65.25

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},

[CPC] = 0.003 mol dm^{-3}

Table-19: Variation of rate constant with DL-alanine concentration at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
[Ala]/M	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$
0.02	13.81	17.27	23.99
0.05	23.99	32.62	38.38
0.15	49.89	65.25	85.36

$[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},
$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},
[CPC] = 0.004 mol dm^{-3}

Table-20 : Variation of rate constant with $[H^+]$ at different temperatures in the presence of CPC.

Temp. (°C)	30	35	40
$[H^+]$/M	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$	$^{+1}k_{obs} \times 10^4/s^{-1}$
0.15	16.31	21.11	28.78
0.10	22.09	26.86	38.38
0.075	25.91	34.54	46.06
0.05	32.62	42.22	57.57

[Ala] = 0.15 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},
$[Na_2S_2O_3]$=5 x 10^{-3} mol dm^{-3}, μ = 0.15 mol dm^{-3},
[CPC] = 0.002 mol dm^{-3}.

On the basis of above data the following kinetic rate law may be proposed

$$-\frac{d\,[CAT]}{dt} = {}^{2i}k\,[\text{amino acid}]\,[CAT] \quad \text{---------- (1)}$$

where ${}^{2i}k$ is the second order rate constant in the absence of any surfactat is represented as ${}^{02}k$ and in the presence of SDS as ${}^{-2}k$ and in the presence of CPC as ${}^{+2}k$.

$$-\frac{d\,[CAT]}{dt} = \{{}^{2i}k + {}^{1i}k/[H^+]\}\,[\text{amino acid}]\,[CAT] \quad \text{----- (2)}$$

where ${}^{1i}k$ is the first order rate constant.

The above equation have been found to be in conformity with the mechanism proposed in scheme I, II, III and IV.

(a) In the absence of any surfactant

$$AH^+ \underset{}{\overset{K_A}{\rightleftharpoons}} A + H^+ \quad \text{--------} \quad (1)$$

$$OXH \underset{}{\overset{K_O}{\rightleftharpoons}} OX + H^+ \quad \text{--------} \quad (2)$$

$$A + OXH \xrightarrow{k_1} \text{-------} \quad \text{--------} \quad (3)$$

$$A + OX \xrightarrow{k_2} \text{-------} \quad \text{--------} \quad (4)$$

$$AH^+ + OXH \xrightarrow{k_3} \text{-------} \quad \text{--------} \quad (5)$$

(Scheme I)

The corresponding rate equation is

$$\text{reaction rate} = \left\{\frac{k_1K_A + k_4K_O}{(K_A + K_O)} + \frac{k_2K_AK_O}{(K_A + K_O)} \cdot \frac{1}{[H^+]}\right\}[A]_0\,[OX]_T$$

(b) In the presence of SDS

$$AH^+ \overset{K_A}{\rightleftharpoons} A + H^+ \qquad \text{--------} \qquad (1)$$

$$OXH \overset{K_O}{\rightleftharpoons} OX + H^+ \qquad \text{--------} \qquad (2)$$

$$OX + S^{n-} \overset{K_S}{\rightleftharpoons} (OXS)^{n-} \qquad \text{--------} \qquad (3)$$

$$OXH + S^{n-} \overset{K'_{OS}}{\rightleftharpoons} (OXHS)^{n-} \qquad \text{--------} \qquad (4)$$

$$A + OXH \xrightarrow{k_1} \text{-------} \qquad \text{--------} \qquad (5)$$

$$A + OX \xrightarrow{k_2} \text{-------} \qquad \text{--------} \qquad (6)$$

$$AH^+ + OXH \xrightarrow{k_3} \text{-------} \qquad \text{--------} \qquad (7)$$

$$AH^+ + OX \xrightarrow{k_4} \text{--------} \qquad \text{--------} \qquad (8)$$

$$A + (OXS)^{n-} \xrightarrow{k'_2} \text{------} \qquad \text{--------} \qquad (9)$$

$$A + (OXHS)^{n-} \xrightarrow{k'_1} \text{--------} \qquad \text{--------} \qquad (10)$$

Scheme-II

The corresponding rate equation is

$$\text{reaction rate} = \{(k_1K_A + k_4K_O + k'_1K_AK'_{OS}\,[S^n]) + \frac{k_2K_AK_O + k'_2K_AK_OK_{OS}\,[S^{n-}]}{[H^+]}\} \frac{[A]_0\,[OX]_T}{(K_A+K_O)+(K_AK'_{OS}+K_OK_{OS})\,[S^{n-}]}$$

(c) In the presence of CPC for glycine

$$AH^+ \underset{}{\overset{K_A}{\rightleftharpoons}} A + H^+ \qquad \text{--------} \qquad (1)$$

$$OXH \underset{}{\overset{K_O}{\rightleftharpoons}} OX + H^+ \qquad \text{--------} \qquad (2)$$

$$OXD \underset{}{\overset{K_d}{\rightleftharpoons}} OX + D^+ \qquad \text{--------} \qquad (3)$$

$$OXD + S^{m+} \underset{}{\overset{K_{OS}}{\rightleftharpoons}} (OXDS)^{m+} \qquad \text{--------} \qquad (4)$$

$$A + OXH \xrightarrow{k_1} \text{------} \qquad \text{--------} \qquad (5)$$

$$A + OX \xrightarrow{k_2} \text{------} \qquad \text{--------} \qquad (6)$$

$$AH^+ + OXH \xrightarrow{k_3} \text{------} \qquad \text{--------} \qquad (7)$$

$$AH^+ + OX \xrightarrow{k_4} \text{-------} \qquad \text{--------} \qquad (8)$$

$$A + (OXDS)^{m+} \xrightarrow{k'_5} \text{-------} \qquad \text{--------} \qquad (9)$$

Scheme-III

The corresponding reaction rate is

$$\text{reaction rate} = \left\{ (k_1K_A + K_4K_O) + \frac{k_2K_AK_O + k'_5K_AK_OK'_{OS}\,[D_0]\,[S^{m+}]}{[H^+]} \right\} \frac{K_d\,[A]_0\,[OX]_T}{(K_A + K_O + K_OK'_{OS}\,[D_0]\,[S^{m+}])k_d}$$

or

$$\text{reaction rate} = {}^{+2}k_G\,[A]_0\,[OX]_T$$

(d) In the presence of CPC for DL-alanine

$$AH^+ \underset{}{\overset{K_A}{\rightleftharpoons}} A + H^+ \qquad \text{--------} \qquad (1)$$

$$OXH \overset{K_O}{\rightleftharpoons} OX + H^+ \qquad \text{--------} \qquad (2)$$

$$OXD \overset{K_d}{\rightleftharpoons} OX + D^+ \qquad \text{--------} \qquad (3)$$

$$OXD + S^{m+} \overset{K_{OS}}{\rightleftharpoons} (OXDS)^{m+} \qquad \text{--------} \qquad (4)$$

$$A + OXH \xrightarrow{k_1} \text{-------} \qquad \text{--------} \qquad (5)$$

$$A + OX \xrightarrow{k_2} \text{-------} \qquad \text{--------} \qquad (6)$$

$$AH^+ + OXH \xrightarrow{k_3} \text{--------} \qquad \text{--------} \qquad (7)$$

$$AH^+ + OX \xrightarrow{k_4} \text{-------} \qquad \text{--------} \qquad (8)$$

$$A + (OXDS)^{m+} \xrightarrow{k'_5} \text{-------} \qquad \text{--------} \qquad (9)$$

$$(OXDS)^{m+} + H_2O \xrightarrow{k'_{H_2O}} \text{-------} \qquad \text{--------} \qquad (10)$$

Scheme-IV

The corresponding reaction rate is

$$\text{reaction rate} = \left\{ (k_1 K_A K_d + K_4 K_O K_d) + \frac{k_2 K_A K_O K_d + k'_5 K_A K_O K_{OS} [D_0] [S^{m+}]}{[H^+]} \right\} \frac{[A]_0 [OX]_T}{D'_S} + k_S [OX]_T$$

The observed results justify all major kinetics features.

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KINETICS OF MICELLES CATALYZED REACTIONS

THESIS

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IN

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BY

FARHAT HASAN KHAN

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

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DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH—202002

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CERTIFICATE

I certify that the work of **Mr. Farhat Hasan Khan** on ***"KINETICS OF MICELLES CATALYZED REACTIONS"*** has been carried out under my supervision. He is allowed to submit his thesis for the consideration for the award of the degree of Doctor of Philosophy in Chemistry.

(PROF. FIROZ AHMAD)

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(FARHAT HASAN KHAN)

DEDICATED

TO MY BELOVED PARENTS,
BROTHERS, SISTERS

AND

TO RESPECTED SIR

CONTENTS

GENERAL INTRODUCTION

MICELLES

MICELLES

It is well known that number of substances in solution lower its surface tension. These substances are called the surface active agent or surfactants. The most commonly known surface active agents are soaps. The detergents are made up of two parts (a) the hydrophilic or the ionic part which is attracted towards water molecules and because of their polarity they are water soluble and (b) the lipophilic part which is polar and is repelled by water molecules. These surfactants are categorized on the basis of the chemical structure of polar group as cationic, anionic, nonionic and zwitterionic. The surfactant molecules in solution aggregate to form micelles depending upon the concentration of the monomer, the lowest concentration at which micelle is formed is called critical micelle concentration (cmc). For any particular surfactant the value of cmc depends upon temperature, hydrocarbon chain types of head groups and nature of additive if any. The micelles are in a state of dynamic equilibrium with varying number of monomers forming the aggregate at different concentrations. Typically the micelles are considered to be spherical with a core structure of nonpolar chain called core whereas the hydrophilic head group faces the water medium lying in the stern layer as shown in the figure 1.

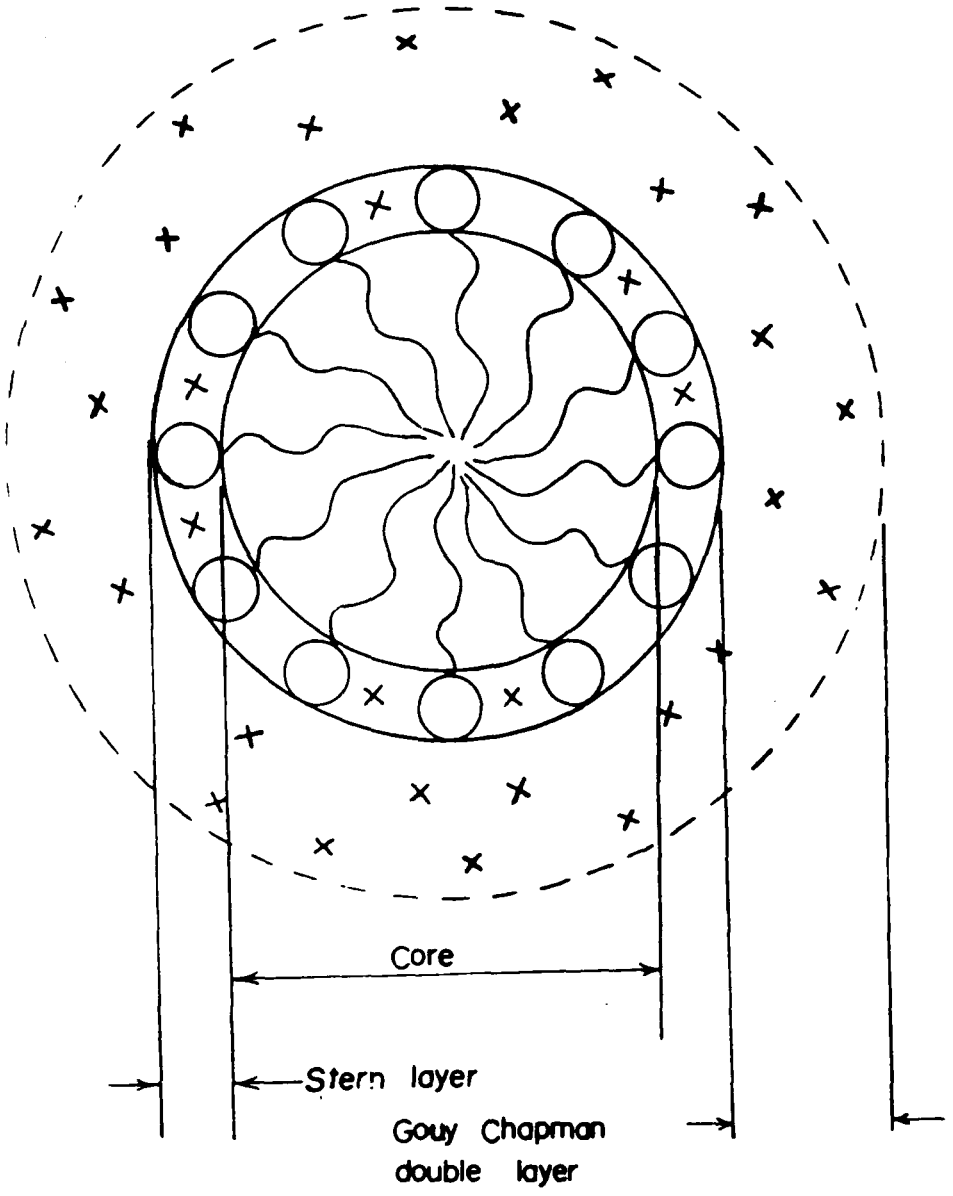


Fig. 1 : A two-dimensional schematic representation of the regions of a spherical ionic micelle. The counterions (X), the head groups(◯), and the hydrocarbon chains (∿∿) are indicated.

The Poisson-Boltzmann equation[1] (PBE) has been used to calculate the surface electrical potential of ionic micelles by solving the PBE in spherical symmetry with the inclusion of specific, noncoulombic binding terms. For solving the PBE the following approximations were made (i) micelles are assumed to be smooth uniform spheres (ii) ions are assumed to be point charges (iii) all reactions are assumed to take place in the stern layer which is assumed to have uniform thickness.

APPLICATION OF MICELLES :

In view of the polar and nonpolar character of micelles a number of applications of the surfactants have been found to be useful in industries, biological system and daily life material. One of the most important useful properties of micellar system is exhibited in their ability to solubilize a number of non ionic chemical species which would otherwise be insoluble in aqueous medium. Generally speaking, the solubilization is possible because of non-polar micro-environment provided by the core groups of micelles within the aqueous medium. The solubilization site depends upon nature and structure of solute[2-4]. These solubilization sites exit in a rapid equilibrium between various possible sites on one hand and between the solubilized state and free state of the solute

in bulk on the other. At times the solubilization in reverse micelles is also found to play an important part particularly in removing polar dirt from cloths. It is also noted that micelles in non aqueous media may be used in motor oils to solubilize corrosive oxidation products. A number of agrochemicals are solubilized as micellar solutions in agricultural sprays and dyeing media. The micellar solutions have been found very effective in removal of odour from factories of food packaging plants. Solubilization of coloured impurities in paper industries and the use of micellar solutions in photographic processes is also well known. In the emulsion polymerization process the solubilization of monomer is made possible in the micellar core. The micellar system provides an extraordinary opportunity in the field of organo-electro-synthesis[5,6]. The other potential application of micellar system are (a) inhibiting the corrosion[7] (b) improving recovering[8,9] of oil products and (c) conversion of light energy into chemical energy which can be used for storage of solar energy in a useful form[10,11].

Ionic micelles exhibit the general features of membrane surfaces[12-15]. Alenxander and Trim[16] as shown demonstrative the surface active molecules may interact

with bactericides and at micellar concentration may inactivate the active species by solubilization. The selective solubilization of membrane components has been exploited to study its structure and functions. It has been observed sodium dodecyl sulfate protein complex can solubilize cholesterol[17]. The biological application of surfactant has been found in the role it place in altering transport across membrane in biological system. It has been noted that the low concentration of polysorbate-80 an other nonionic surfactants results enhancing the permeability of membranes and this effect is maximal at cmc. The surfactant are added to drugs as emuslsifiers, suspending and wetting agents. In this regard, the relative affinity of drug for micelles incomparison to the membrane is an important factor of biological control of absorption drug. The partition coefficient and transport parameters of drug depends on cmc value of the surfactant, it may be noted that high concentrations surfactant may cause tissue damage and also decrease the thermodynamic activities of drug[18].

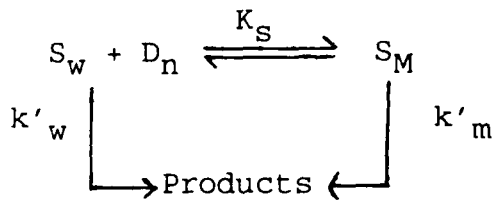
THE ROLE OF MICELLES IN KINETICS

In view of great similarity with the enzyme catalyzed reaction[19-22] the surfactant catalyzed reactions have attractive interact of number of researchers. The

similarities of the two reaction are based on (a) both have similar structure containing hydrophobic core and polar group, (b) both bind the reacting substrate through non covalent bond and (c) the rate constant of micelle catalyzed reactions follow sigimoid shaped curve.

The catalytic effect of micelles has been attributed to the fact that micelles bring the reacting molecule in close proximity (generally in the stern layer). On the other hand the inhibition may be observed due to adsorption of one reactant and repelling of the other by the polar micellar surface. In view of the fact that the cmc of the surfactant depend on the other factor such as the pH and temperature, and sometime the values of kinetic cmc may be different for a particular system from the experimentally determine in a non kinetic suitation. As studied above the solubilization of nonpolar substrate in the presence of surfactant was the major source of attraction to study the kinetic of the organic reaction in the micellar system. However, recently inorganic[23,24] reaction also have been studied. The reactions occurring in the micellar system are treated interm of pseudophase model where in the micelle and water presence are regarded as distinct phases. The distribution of substrate between aqeuous and micellar phases is expressed in terms of Michaelies Menten type equation[25-30]. Menger[31]

has proposed a pseudophase kinetic model for micelle catalyzed reaction which has been further developed by Bunton[32] and Romsted[33]. The proposed mechanism is



Scheme

Where M and W denote the micellar and aqueous pseudophase respectively. S is the substrate, D_n is the micellised surfactant (Where D_n = [D] - cmc/N) and K_S is the binding constant of the substrate to micelles and is given by

$$K_S = [S_M]/[S_w]\ [D_n] \text{ ---------- (1)}$$

In confirmation with the above scheme the following rate equation was observed.

$$K_\psi = k'_w + k'_m K_S\ [D_n]/1+K_S\ [D_n] \text{ ------ (2)}$$

equation (2) hold for the unimolecular reaction occurig in the micellar system.

Bunton and Robinsion[34] studied the hydrolysis of 2,4-dinitrochlorobenzene in water or aqueous alcohol medium in presence of surfactant. They observed that the reaction was catalyzed by cationic micelles of

cetyltrimethylammonium bromide (CTAB) and retarded by anionic micelles of sodium dodecyl sulfate (SDS) but a nonionic micelle had no effect. The rate constant, in the presence of CTAB, shows a maximum, the kinetic features were interpreted quantitatively in terms of incorporation of substrate and hydroxide ion into the cationic micelles. The parameters derived by measurements of solubilization of substrate showed that the detergents are affecting the reaction rate by incorporating the substrate into the micellar aggregate, rather than by changing the solvent properties of the water. Other workers have proposed similar mechanism[35-42]. It appears that the cationic micelle decrease the activation energy and anionic micelles increase it.

Romsted and Cordes[43] reported the effects of n-alkyltrimethylammonium halide surfactants on the alkaline hydrolysis of p-nitrophenyl acetate, p-nitrophenyl hexanoate and p-nitrophenyldodecanoate. No enhancement in the reaction rate was observed in solutions of in surfactant concentration range of 0.4 and 0.2 M, however, at lower concentration of surfactant in the range of 10^{-3} to 10^{-2} M marked increase in the reaction rate was observed. Furthermore, when the n-alkyl group chain contained twelve or more carbon atoms the magnitude of the

catalysis was found to increase with increasing chain length of the surfactant for all three esters. The orders of reactivity of the esters in each micellar solution was found to be p-nitrophenyl dodecanoate > p-nitrophenyl >> p-nitrophenyl acetate which establishes a relationship between the hydrophobic chain length of the carbonyl group and the magnitude of micellar catalysis.

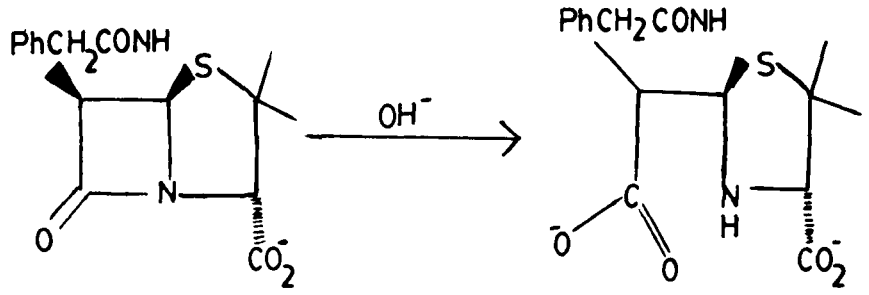
Zeffren and Watson[44] observed that the anionic surfactants caused marginal retardation in reaction rate of the neutral hydrolysis of p-nitrophenyl acetate. The nonionic micelles had negligible catalytic effects (by introducing neuclophilic group into the surfactant). They have suggested that p-nitrophenyl acetate does not penetrate sufficiently beyond the micellar surface to allow appropriate interaction between the carboxyl group of the ester and the hydroxyl group of the micelle. The similarities of the observed relative rates of hydrolysis in these nonionic micellar amine oxide surfactants as a functions of chain length of the ester (specifically, p-nitrophenyl acetate, butanoate and hexanoate) substantiates this postulate. It is also probable that the potentially nucleophilic hydroxyl group is oriented at or near the micellar surface hydrated by surrounding water molecules which either dissipates its potential activating effect or prevents orientation in the necessary geometry, i.e. proximity.

Menger and Partnoy[41] reported that anionic micelles of sodium dodecanoate retarded and cationic micelles of dodecyltrimethyl ammonium bromide enhanced the rate of alkaline hydrolysis of n-nitrophenyl acetate, mono-p-nitrophenyl dodecanedioate, and p-nitrophenyl acetanoate. The magnitude of micellar effects becomes greater with increasing hydrocarbon chain length of the substrate.

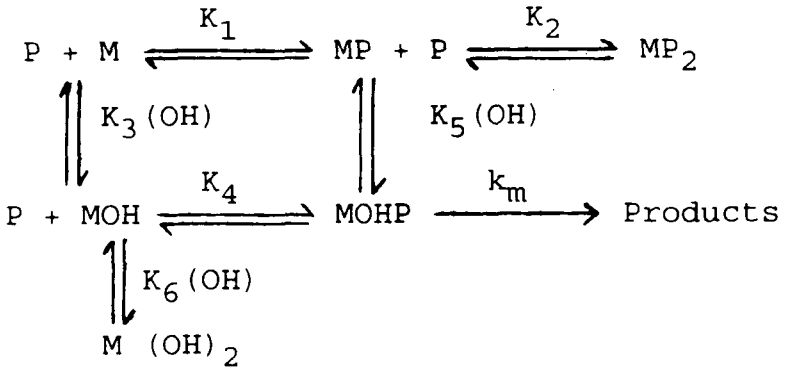
In their studies Behme[37] et al. observed that the magnitude and direction of the effects of cationic, anionic, and neutral micelles on the rate of aminolysis of p-nitrophenyl acetate and hexanoate by leucine and morpholine differ considerably in some cases from those on the rate of hydrolysis of these substrates. For p-nitrophenyl hexanoate, the rate of aminolysis by morpholine is retarded by all three types of surfactants while that by leucine is considerably accelerated by cationic surfactants and retarded by anionic and neutral ions.

The Kinetic effect of micelles has been predictable on the basis of electrostatic interaction, the hydrophobic substrate and counterions are attracted to the micelles, therefore, the cationic micelles catalyzed the reaction between a neutral molecule and anionic nucleophile while anionic micelles inhibited such reactions. Gensmantel and Page[45] studied the reaction between two anions, the

hydroxide ion catalyzed hydrolysis of negatively charged benzylpenicillin.



Micelles of SDS, polyoxyethene lauryl ether show no effect of the rate of hydrolysis. On the basis of electrostatic considerations, the authors concluded that the benzylpenicillin anion and hydroxide ion were repelled by the anions SDS micelles. The neutral micelles of polyoxyethylene lauryl ether did not effect the rate of hydrolysis due to lack of affinity for hydroxide ion. The CTAB, micelles showed that the pseudo first-order rate constant increased rapidly with surfactant concentration above the critical micelle concentration which shows levelling effect at sufficiently higher surfactant concentrations. On the basis of these studies, they have assumed that both hydroxide ion and penicillin are bonded to the micelle surface for hydrolysis to occur.



Where, P, M and OH refer to the penicillin anion, micelle, and hydroxide ion respectively, while MOH, $M(OH)_2$, MP, MP_2, and MOHP refer to binary or ternary complexes. Only MOHP, the ternary complex between micelle and the two reactant molecules leads to products. Thus, the incorporation of the reactants into a limited volume decreases the loss in entropy in the transition state as reacting ions are already catalyzed. This causes increase in the pseudo first-order rate constants in the presence of surfactant micelles.

Sicilia[46] et al. presented a kinetic method for the determination of sodium dodecyl sulfate (SDS) concentration. The method is based on catalytic effect of micelles on the reaction between iron (II) and 1, 10-Phenanthroline. Triton X-100 micelles have no catalytic effect on the reaction. The mixed micelles, formed by adding triton X-100 to SDS, catalyzes the reaction event at very low SDS concentration. The

proposed method was applicable for the direct determination of the surfactant in shampoos, toothpaste and rectal solution. Thus, this method of enhancement in rate of reaction provides convenient experimental method and use of organic solvent can be also avoided.

Broxton and Lucas[47] studied the reaction of several nitro-activated aromatic halides with hydroxide ion in the presence of hydroxy-functionlized micelles containing bulky head group such as $C_{16}H_{33}N^{+}R_2CH_2CH_2OHBr$ (R = Me, Et, Bu). In a biphasic reaction, the aryl halide is first converted to an aryl micellar ether, which subsequently reacts with hydroxide ions to form the phenolic product. Despite the increased nucleophilicity of hydroxide ions as water is squeezed away from the micelle surface by the bulky head groups, no direct reaction of the aromatic substrate with hydroxide ions is detectable. In the second phase of reaction, the breakdown of the aryl micellar ether to form the phenolic product take place the order of reactivity in the different micellar system is dependent on the steric interactions between substituents ortho to the reaction centre and head group of the reaction centre, the order of reactivity is Bu > Me > Et. For 2-chloro-1, 3-dinitrobenzene, however, which has two substituents ortho to the reaction centre, the order is Me > Et > Bu.

Itoh Shingo[48] et al. observed that the rate constants quenching of singlet oxygen (k_Q) by α-, β- , γ- , and δ-Toc-amines increased as the total electron donating capacity of the methyl group at the aromatic ring increased. A plot of log k_Q Vs. peak oxidation potential (E_p) in the presence of Triton X-100 was found to be linear with negative slope. Similar results were obtained for scavenging of a phenoxy radical (Pho). The results suggest that charge transfer plays an important role in these reactions.

Cuenca and Bruno[49] studied the effect of cationic micelles of alkyltrimethyl ammonium chloride and bromide (alkyl = n-$C_{12}H_{25}$, n-$C_{14}CH_{29}$ and n-$C_{16}H_{33}$ and anionic micelles of sodium dodecyl sulfate upon hydrolysis of 2-phenoxyquinoxaline. They observed that the cationic micelles catalyzed the reaction while anionic micelle inhibited. The results were treated quantitatively by considering the pseudo-phase ion exchange model and found that the second order rate constants in the micellar pseudo-phase are similar to the second order rate constants in water.

Curamato and Genies[50] studied the chemical oxidative polymerization of aniline in an aqueous SDS micellar system. The polymerization proceeded rapidly

resulting in a homogeneous emeraldine coloured disperson of polyaniline at about pH 7-8 in anionic micellar system.

The condensation reactions of acetophenone cyclohexanons, isophorone, phenyl acetonitrile, (p-nitrophenyl) acetonitrile (phenyl sulfonyl) acetonitrile and indene benzaldehyde were studied by Fringuelli[51] et al. in water in a heterogeneous phase in presence and absence of anionic and cationic surfactants of SDS, and several other surfactancts. The cationic surfactants favoured the reaction, and comparison with the corresponding tetrabutyl ammonium salts showed that micellar catalysis was effective mainly in the dehydration reaction following the condensation. The anionic surfactant was inactive.

Sankararoz[52] et al. observed that the anionic surfactant, SDS, catalyzed the redox reaction of dialkyl sulfides with chromium (VI), while the rate of this reaction was inhibited by the cationic surfactant, CTACl. They have assumed that the reaction takes place both in aqueous and micellar phases. The catalytic role of $[H^+]$ and development of positive charge on sulfur due to the electron transfer from sulfide to Cr (VI) favoured the reaction in the anionic micelle and was disfavoured in the presence of cationic micelles.

Oxidative cleavage of 2-amino-4-methyl pentanoic acid by cerium (IV) perchlorate in perchloric acid medium in the presence of several surfactancts has been reported by Mishra and Nand[53]. The reaction follows second order kinetics, being unity in each of the reactants. The catalytic action is triton X-100 > SDS > TEABr > CTAB. A mechanism consistent with kinetic data has been proposed which permits the evolution of theoretical values of the rate constants.

Favaro Reinsborough[54] reported the dye solubility in the mixed surfactant system sodium dodecyl sulfate/dodecyl trimethyl ammonium bromide with excess of anionic surfactant and used stopped flow technique for kinetic studies. The enhanced rate in the presence of anionic micelles of the Ni^{2+} (aq)/pyridine -2-azo-p-dimethylaniline (PADA) complexation reaction was used as a probe of the mixed micellar situation. PADA solubilities and the Kinetic parameters derived on the basis of Robinson model for micellar catalysis were consistent.

Yamashita[55] et al. studied the effect of micelles on the kinetics of the ionization of basic (arginine) and acidic (aspartic acid) amino acids by the ultrasonic absorption method. The values of forward ($\gamma^2 k_f$), and backward (k_b) rate constants, the apparent base dissociation constant K_b ($k_b/\gamma^2 k_f$), and the volume change

(ΔV) for the reaction were obtained. The effect of SDS micelles on arginine was greater than those for neutral amino acid, while the effect of cationic micelles of dodecylammonium chloride (DAC) on aspartic acid was found to be slightly lower than that for an aromatic carboxylic acid-DAC system.

Vera and Rodenas[56] studied the basic hydrolysis of acetyl salicylic acid in CTAB micelles. The increase in temperature increased the micellar rate constant and on the basis of these results, the values of apparent activation energy was also determined.

Khan[57] et al. observed that the pseudo first order rate constant for the base catalyzed hydrolysis of methyl salicylate (MSH) which was found to be almost independent of SDS concentration while those for phenyl salicylate obeyed the rate equation.

$$k_{obs} = \frac{(k_w + k_M K [D_m])}{(1 + K [D_n])}$$

On the basis of their studies, they proposed that the micelle is a porous cluster with a rough surface.

The studies[58] on the effect of non-ionic micelles (alkylpoly oxyethylene glycol monoether) on the kinetics of the electron-transfer reactions of iron (III) with

substituted ferrocenes (Bu, 1, 1'-dimethyl, and 1,1'-dibutyl derivatives) revealed that the non-ionic micelles retard the electron transfer reaction. The inhibiting micellar effects are markedly dependent on the hydrophobicity of the reducing species and, to a lesser extent, on the type of micelle forming surfactants. The reactivity data, the estimated binding constant, and the standard transfer free energies of ferrocenes from H_2O to the micelle suggest that binding of the solubilizates occurs in the hydrocarbon interior of the micelle.

Khan[59] et al. reported that $[SDS]_T$ micelles resulted in decrease of rate of aminolysis of phenyl salicylate (PS) and methyl salicylate (MS). At high $[SDS]_T$ plots of observed pseudo -first order rate constants (k_{obs}) versus total propylamine concentration ($[Am]_T$) exhibit smaller slopes at $[Am]_T < 0.01$ moldm^{-3} compared with those at $[Am]_T > 0.01$ moldm^{-3}. These observation are attributed to the higher hydrophilicity of 1-aminopropan-2-ol compared with that of propylamine. The values of k_n for hydrazinolysis of MS^- decrease 1.7 fold and those for hydroxylaminolysis of MS^- doubled at 0.2 moldm^{-3} in this concentration range of $[SDS]_T$. The values of $[SDS]_T$ are within the limits 0.0-0.2 moldm^{-3}. $[SDS]_T$ dimethylamine did not show any detectable nucleophilic reactivity towards MS^-. This show that the presence of

SDS perhaps does not change the nucleophilic reaction mechanism of aminolysis of salicylate esters. The observed results of aminolysis of PS^- and MS^- are rationalized in the light of the proposal of a porous cluster micellar structure.

Archontaki[60] et al. described a kinetic potentiometric method for the determination of phenol and phenolic drugs based on monitoring their reaction with 1-fluaro-2, 4-dinitrobenzene, catalyzed by cetyltrimethyl ammonium bromide micelles using a fluoride-selective electrode. Micelles enhanced the reaction of the various phenolic compounds several times.

Lohedan[1] studied the basic hydrolysis of tert-butyl perbenzoate and 2-naphthyl benozate in the cationic micelles of cetyltrimethylammonium surfactant [CTA(X), X=C1, Br, OMS] and reported an increase in first order rate constants. Dealkylation of both butyl 4-nitrobenzene-sulfonate and butyl 4-bromobenzenesulfonate by halide ions in micelles of CTACl, CTABr, and CTAOMs by azide ion as well as the nucleophilic aromatic substitutions of 2-chloro-3, 5-dinitropyridine by OH^- and N_3 ions in the presence of CTABr, CTACl and CTAOMs micelles have been examined. The rate enhancements have been treated in terms of concentration of both substrates and nucleophilic

anions at the micellar surface by applying a model that accounts for the both coulombic and specific interactions of ions with aqueous ionic micelles.

Berndt[61] et al. observed that the order of reaction for the alkaline hydrolysis of various hydroxamic acids in the presence of cetyltrimethyl ammonium bromide (CTAB) were different depending upon the reaction conditions and substrate used. The kinetic results followed the Michalies-Menten rate equation.

Micelles formed by the copper (II) complex of N, N, N'-trimethyl-N'-tetradecylethylenediamine[62] showed 25 times rates enhancement of cinnamoyl fluoride relative to the reaction in the micelles of hexadecyltrimethylammonium chloride. The aggregation of the copper (II) complex was essential in promoting the reactivity as the monomeric copper (II) complex of N, N, N', N'-tetramethylethylenediamine had very little effect on the hydrolysis rate.

The kinetic and equilibrium for the complexation reactions of iron (III) with bidentate ligands 4-ethyl and 4-butyl amino-2-hydroxybenzoic acids were studied by Cavasino[63] et al. in aqueous acidic solutions containing varying concentrations of non-ionic micelles (Briz-35). The results indicate that the complexation reaction occurs in the aqueous micelle interphase. The binding constants of the Fe (III) mono complexes and the neutral ligands to

nonionic micelles were also established from the equilibrium and kinetic data.

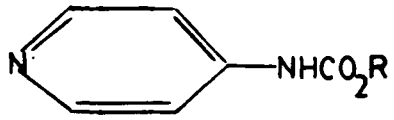
Islam[64] et al. compared the activity of nonionic micellar system and human serum albumin (HSA) by studying the rate of reaction of cis and trans (conversion of some diol epoxides called DE-1 and DE-2) in solution containing HSA and Tween-80. The effect of increasing concentrations of both HSA and Tween-80 is to retard substantially the rates of reaction of DE-1 and DE-2 over the pH 5-7. The rate data are consistent with a mechanism in which the diolepoxides physical association with HSA or Tween-80, and the rates of reaction of the association complexes are reduced compared to those of free diol epoxide. The limiting rate constants for reaction of the diol epoxide HSA and diol expoxide. Tween-80 complexes are dependent on pH. The rates are best accommodated by a mechanism in which the complexes react by 2 competing pathways ; one whose rate is proportional to hydronium ion activity, and the second whose rate is pH-independent. These reactions are, therefore, kinetically analogous to the acid-catalyzed and spontaneous reactions of the (DE-2). HSA complex results in ~ 10% of covalent binding of diol epoxide to the protein, whereas, the acid catalyzed reaction of the complex results in significantly less covalent binding.

The hydrolysis of aspirin in solution at various pH values and in the presence of increasing concentration of sodium dodecyl sulfate (SDS) was investigated by Ismail and Simonelli[65] at 35°. The hydrolysis followed first order kinetics. The presence of SDS results in protection of aspirin against hydrolysis. It was assumed that as the surfactant concentration was increased, aspirin was distributed in a micellar phase and the amount of aspirin present in the true aqueous phase, which is susceptide to hydrolysis was reduced. The data revealed that the presence of SDS did not alter the optimum pH value for the stability of aspirin solution which was found to be 2.4.

The studies[66] on the reactions of chloride (Cl^-) and bromide (Br^-) with substituted alkyl benzenesulfonate in micelles of cetyltrimethylammonium sufractant (CTAX ; X = Cl, Br, OSO_2Me, 0.5 SO_4) shows that the rate increases monotonically with increasing [CTACl] or [CTABr] or halide ion concentration and acquires limiting values at higher concentration. However,with $CTAOSO_2Me$ or $(CTA)_2SO_4$, the rate constants pass through maximum. The variation of the rate constants with concentration of surfactant and halide ion can be fitted to an equation that accounts for the distribution reactants between water and micelles.

The kinetic of complexation of Ni^{2+} by 8-quinolinol (oxine) was investigated in neutral (Triton-x-100 and Brij-35) cationic (CTAN), and anionic [SDS] micelles. Muralidharan[67] et al. interpreted the kinetic result by using the distribution model, considering concurrent pathways for the complexation of Ni^{2+} by neutral oxine and its anion both in the aqueous and the micellar phases. The relevant distribution constants of the species involved were determined independently by spectrophotometric measurements. The distribution constants of the neutral oxine in the micelles suggest that it resides in the hydrocarbon portion of the micelles. The oxine anion exhibits a greater acceleration units interaction with Ni^{2+} than the neutral oxine. The kinetic data indicate that the complexation reactions occur in bulk aqueous and the micellar phases, and that there is no contribution from the aqueous micellar interface.

The kinetics of hydrolysis of pesticidal such as N-(4-pyridyl) carbamates I (R = Ph or Me) were studied by Matondo[68] et al. in micellar H_2O - dioxane solutions



(I)

containing SDS or CTAB. The reaction was slightly inhibited by the SDS and catalyzed by the CTAB micelles

for I (R=Ph) whereas a decrease in the reaction rate was observed for I (R=Me). The results were interpreted by considering pseudo phase kinetic model coupled with the hydrolysis mechanisms of these compounds in water dioxane solution.

The complexation of iron (III) with SCN^- was investigated in aqueous micellar media by Dash and Mohammed[69]. The rate of reaction decrease 400 times in SDS. The major path of dissociation of the complex monothiocyanatoiron (III) in the anion micellar pseudo phase is

$$Fe(OH)\ NCS^+ \longrightarrow Fe\ (OH)^{2+} + SCN^-$$

This reaction is moderately accelerated by the anionic micelles. The neutral micelles of Triton X-100 have little effect on the rate of formation and dissociation of $FeNCS^{2+}$ or $Fe(OH)NCS^+$.

Reinsborough[70] et al. used mixed micelles of sodium-perfluorooctanoate (spfo) and sodium octanesulfonate (sos) for the kinetic studies of the complexation of Ni^{2+} with the bidentate ligand. The unexpected effectiveness of spfo in the rate enhancement is due to its compact micellar reaction volume of o.16 $dm^3\ mol^{-1}$. The kinetic

results are consistent with spfo and sos forming separate micelles.

Zhang[71] et al. evaluated the kinetic parameters of complex formation between Ni (II) and neutral terdentate ligand 2,2",2"- terpyridyl (Terpy) in the presence of SDS micelles. In SDS micellar solution under pseudo-first order condition, the rate determining step of reaction is the release of H_2O molecule from the inner co-ordination sphere. The apparent activation energy of the reaction has been estimated.

A detailed kinetic analysis of purified yeast membrane associated phosphatidate phosphate was performed by Lin and Carman[72] using Tritin X-100/ phosphatidate mixed micelles. Enzyme activity was dependent on the bulk and surface concentration of phosphatidate. These results were consistent with the surface dependent kinetic scheme. Phosphatidate phosphatose binds to the mixed micelle surface before binding to its substrate and catalysis occurs subsequently. Phosphatidate phoshatose was shown to associate with Triton X-100 micelles in the absence of phosphatidate, however, the enzyme was more tightly associated with micelles when its substrate was present. The enzyme had 5 to 6 fold greater affinity (reflected in the dissociation constant nK_sA/x for Trition X-100 micelles. The V_{max} for dioleoyl-phosphatidate was higher

the V_{max} for dipalmitoyl-phosphatidate, whereas, the interfacial Michaelies constant xK_mB for dipalmitoyl-phosphatidate was 3 fold lower than the xK_mB for dioleoyl-phosphatidate. The specificity constant (V_{max}/xK_mB) of both substrates were similar which indicated that dioleoyl-phosphatidate and dipalmitoyl-phosphatidate were equally good substrates.

Dash[73] et al. studied the effect of neutral and anionic micelles on the kinetic of equation and base hydroysis of some cis-(chloro) (amine) bis (ethylenedia mine) cobalt (III) complexes. The binding of the substrate cis-$[Co-(en)_2BCl]^{2+}$ (B = alkylamines, imidazole, N-methylimidazol) to the SDS micellar surface resulted in the retardation of their dissociative equation rates, the effect being sensitive to the hydrophobicity of the nonlabileamine ligand B. For the corresponding ethanolamine and isopropanolamine complexes smaller acceleration in the rate was observed. Trition X-100 ($0.02 \leq [Triton]_T/moldm^{-3} \leq 0.1$) had virtually no effect on thc equation rates of such complexes except for cis- $[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$. The rate of base hydrolysis of the Co(III) substrates were retarded strongly by the anionic micelle of SDS, the neutral micelles of Trition X-100 were effective in retarding the rate of base hydrolysis of the

cyclohexylamine complex cis-$[Co(en_2)\ (C_6H_{11}NH_2)Cl]^{2+}$ only. The pseudo-phase ion exchange equilibrium model satisfactorily explained the binding of the cationic substrates to the anionic micellar pseudophase of SDS. The values of the ion-exchange equilibrium constant and the relative base hydrolysis rates (k_w/k_m) indicated that both micellar binding and retardation of hydrolysis are governed by hydrophobic and electrostatic interactions.

Germani[74] et al. studied the effect of head group size on the rate of decorboxylation of 6-nitrobenzisoxazole-3-carboxylate ion. They observed that the rate and decorboxylation increased sharply with increasing head group size in a series of cetyltrialkylammonium bromide ($C_{16}H_{33}NR_3Br$; R = Me, CTABr ; R = Et, CTEABr ; R = Pr, CTPABr ; R = Bu, CTBABr) ranging from 10^2 (CTABr) to 2.8×10^3 (CTBABr). These differences in catalytic efficiency depend on the head group structure and the extent to which the cationic head group become less accessible to water rather than the overall micellar structure.

The base catalyzed dehydrochorination of 1, 1-bis (p-chlorophenyl)-2,2,2-trichloroethanol (Dicofol) in CTAB micelles was studied by Rodenas and Otero[75] at wide range of $[OH^-]$. While at low OH^- concentration, the experimental

pseudo-first order rate constant decreased with surfactant concentration, and at high OH^- concentration the rate constant increased with CTAB concentration. The results were analyzed by means of a pseudophase ion-exchange kinetic model.

The stochastic treatment of reaction kinetics of quenching of an excited probe by a quencher, both solubilized in a micelle were investigated by Tachiya[76]. The three cases are considered concerning migration of probes and quenchers between micelles namely: (1) the case where only quenchers migrate (2) the case where only probes migrate ; and (3) the case where micelles exchange solubilizties by fusion - fission process. The decay cures of the excited probes are calculated for the 3 cases and compared with each other.

Dehydrobrominatin reactions of parasubstituted 2-phenyl ethyl bromides, i.e. P-Y-$C_6H_4CH_2CH_2Br$ (Y-NO_2, Cl, H, OCH_3) have been examined by Wilk[77] in aqueous micelles of the functional surfactant N, N-dimethyl-N-(2-hydroxyethyl)-n-hexadecylammonium bromide (I) in the presence of sodium hydroxide. The kinetic experiments have been performed for a partially deprotonated nucleophilic head group. The variation of the overall first-order rate constant with concentration of (I) and micellar concentration has been explained in terms of ion exchange equilibrium.

Perez and Rodenas[78] studied the catalytic effect of sodium dodecyl sulfate (SDS) micelles on the chromium (VI) oxidation of alcohols in the presence of $HClO_4$. The pseudo-first order rate constants for water soluble alcohols (benzyl alcohol ; 2-propanol, and 1-butanol) increases with SDS concentration showing a maximum, however, but for water insoluble alcohols like 1-hexanol and 1-octanol, the pseudo-first order rate constants show a fall after the maximum with SDS concentrations. These kinetic results were explained by the pseudophase ion exchange kinetic model, by considering that micellar counterions and $[H^+]$ ions complete for the ionic head groups of the micellar surface.

Panigrahi and Sahu[79] studied the effect of cationic micelles of N-dodecyl pyridium chloride on the oxidation of acetophenones by Ce(IV). The surfactant was found to inhibit the reaction. The substrate depletion in the aqueous phase as a result of micellar binding was responsible for further decrease in reaction rate.

Khan[80] observed catalytic effect of anionic micelles on alkaline hydrolysis of N-hydroxyphthalimide. Kinetic data were interpreted in terms of the pseudo phase model and proposed that the reaction occur between the exterior boundary of the layer and the Gouy-chapman layer.

Chimi[81] et al. studied the degradation of kinetic of fatty acids and phenolic compound in micellar medium and observed that micelles of linoleic acid autoxidized almost 10 times these substrates more rapidly than micelles of oleic acid. Micelles composed of a mixture of linoleic acid and oleic acid in a molar ratio of 1:5 showed modified oxidation kinetics. Phenolic compounds retarded the autoxidation rate of the fatty acids. Their antioxidant activity increased in the orders; BHT < tyrosol < caffeic acid < aleuropein < hydroxytyrosol.

Kinetic analysis of the reaction between α - tocopheroxyl radical and ascorbic acid shows that the inter-and intramicellar diffusion may be the rate limiting steps for the reaction carried out in micelles[82]. The life time of the reaction intermediate, ascorbate radical anion, was greatly enhanced by the lipophilic side - chain.

Ismael and Tondre[83] studied the possibilities of metal recovery using micelle-solubilized extractants. The method is based on very slow rate of complexation observed between hydrophobic extractants. The method is based on very slow rate of complexation observed between hydrophobic extractants (7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline) solubilized in cationic micelles (CTAB)

and transition metal ions (esp. Ni^{2+} and Co^{2+}) has been suggested. Achieving a selective separation of metal ions on the basis of differences in their kinetics parameters of complexation. These processes lead to a total removal of CO_2^+ ions.

The kinetics of the substitution reactions between anions ($S_2O_3^{2-}$, SCN^-, Br^-, I^-) and [Pd (N-N-N) X]$^{m+}$, with X being NO_2, Cl and Y giving pararent, methyl and ethyl derivatives, [Pd (N-N-N-Y)X)$^{m+}$ have been studied by cusumano[84] et al. 25° and ionic strength 0.03 moldm^{-3} in water and in the presence of sodium dodecyl sulfate (SDS). All the reactions exhibit a first order dependence on both the substrate and the anion concentration. The substitution rates in water depend on the steric hindrance of the palladium (II) complexes and the nucleophilicity of the entering anions. The presence of SDS retards the reactions because of the binding of the palladium (II) complexes to the anionic micellar aggregates. The binding constants of these complexes estimated from the kinetic data, depend on both the charge of the complexes and the hydrophobicity of N-N-N co-ordinated to the metal.

The oxidation of pyrogallol red (PR) by peroxodisulfate in the presence of dodecyltrimethyl ammonium bromide (DTAB) was further catalyzed by Pb (II)[85]. It is suggested that lead (II) accelerates this reaction by

forming a complex with PR which binds to micellar surface. The micellar catalysis of DTAB can be used for the selective spectrophotometric determination of lead (II) over the range 2-18 ng mL^{-1}.

Bacaloglu[86] et al. studied the effect of micelles on the oxidation of 2-chloroethyl phenyl sulfide (I) by peroxymonosulfate ion (HSO_5^-). Oil micelle-forming cationic surfactants slightly enhance the reaction rate which decrease sharply with increasing surfactant concentration. The second order rate constant in the micellar pseudo phase (k_m) is smaller than k_w in water. These oxidations are retarded by decrease in the water content of aqueous-acetonitrile mixed solvent, and micellar rate effects are consistent with transition states in which positive charge builds up on sulfur.

Sierpinska[87] et al. studied the reaction of colour photographic developer N, N-diethyl-p-phenylenediamine in Triton X-100 micelles and dioctylphthalate emulsion., Quinoidic is reported to be the reactive developer. The reaction rate constant ratio was proportional to the ratio of spherical surfaces of micelles and microemulsion.

Khan and Arifin[88] studied the effects of Li^+ and K^+ ion in the presence of micelles on the rates of intramolecular general basecatalyzed methanolysis of

ionized phenyl salicylate. The pseudo first order rate constant (k_{obs}) for methanolysis of ionized phenyl salicylate (PS^-) decrease 3.5 fold with increase in [CH_3CN]. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are not significantly affected by the presence of CH_3CN in mixed aqueous solvents. The presence of 0.01 $moldm^{-3}$ LiOH, however, causes the increase in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of 3.82 K $calmol^{-1}$ and 10.3 $calK^{-1}mol^{-1}$ respectively. An increase in the total concentration of cetyltrimethyl ammonium bromide ($[CTAB]_T$) from 0.0 to 0.01 $moldm^{-3}$ decreases k_{obs} in the presence of 0.01 $moldm^{-3}$ Li^{3+} and K^+ ion respectively, in mixed aqueous solvents containing.

OXIDATION OF AMINO ACIDS

OXIDATION OF AMINO ACIDS

The oxidation of amino acids is an extremely important and well established bio-chemical, process. However, the mechanism of chemical reaction involved has been not fully established due its diversity and other complications. It is noted that increasing number of research papers are being produced with remarkable and exciting results.

A summary of research work in this field is presented below.

The kinetics of oxidation of some amino acids in perchloric acid with Cl^- ion as a catalyst were studied by Hiremath[89] et al. the results were compared with those obtained with chlorine water and HOCl as oxidant. It is observed that the reaction is first order with respect to 1-chlorobenzotriazole [CBT] and [amino acid] each and fractional order in $[Cl^-]$ and $[H^+]$ ions. A mechanism suitable with the observed kinetics is proposed.

$$SH^+ + H^+ \overset{K_1}{\rightleftharpoons} SH_2^+$$

$$CBT + H^+ \overset{K_2}{\rightleftharpoons} CBTH^+$$

$$CBT\ H^+ + Cl^- \overset{K_3}{\rightleftharpoons} [C]$$

$$[C] + SH^{+} \xrightarrow[\text{Slow}]{k_2} \text{Products}$$

The kinetics of oxidation of α-amino acids by N-chlorosuccinimide (NClS) and N-bromosuccinimide (NBS) in aqueous medium has been investigated by Ramachandran[90] et al. Results show that the observed rate of oxidation is first order in [oxidant] and zero order in [substrate], further perusal of the results suggests that NClS/NBS reacts with α-amino acid anion to produce α-amino acyl hypohalite which then decomposes in the rate determining step. The mechanism proposed is in accordance with observed kinetics.

$$>N\text{---}X + RCH(\overset{+}{N}H_3)COO^{-} \xrightarrow{\text{fast}} RCH(\overset{+}{N}H_3)COOX + >N-$$

X = Cl OR Br

$$RCH(\overset{+}{N}H_3)COOX + OH^{-} \underset{}{\overset{K_1}{\rightleftharpoons}} R\text{---}\underset{\displaystyle NH_2}{\overset{\displaystyle H \text{ ------ } \bar{O}H}{C}}\text{---}COOX$$

$$RCH(NH_2)COOX \xrightarrow{k_1} \text{Products}$$

$$R\text{---}\underset{\displaystyle NH_2}{\overset{\displaystyle H \text{ ----- } \bar{O}H}{C}}\text{---}COOX \xrightarrow{k_2} \text{Products}$$

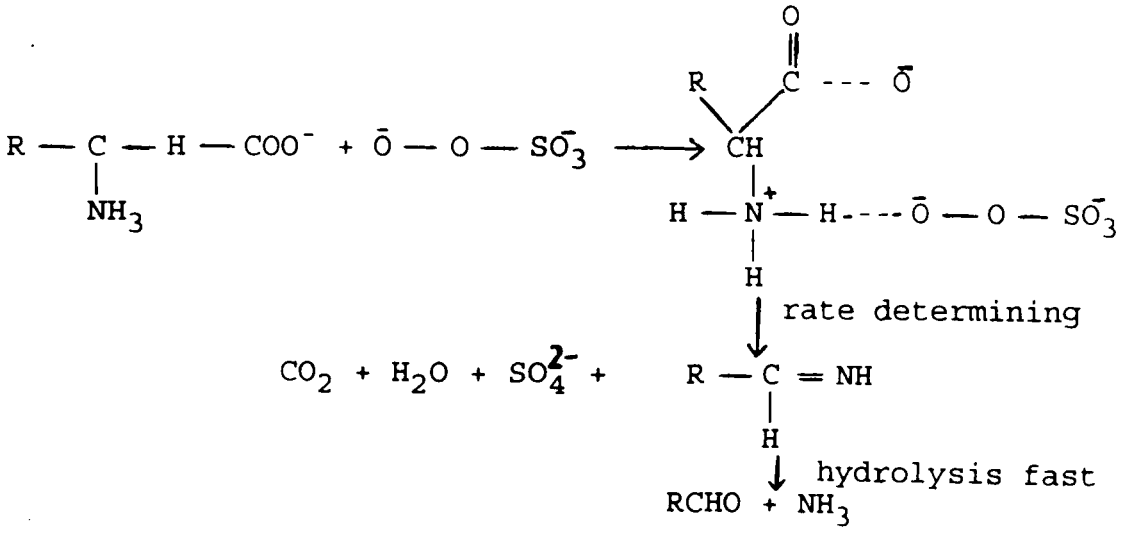
The kinetics and mechanism of the oxidation of amino acids by peroxomonosulfate (PMS) has been studied by Ramachandran and Vivekanandam[91]. The observed rate is first order in [oxidant] and [amino acid] and inverse first order in hydrogen ion concentration. Investigators show that aldehyde, is the oxidation product. The rate expression involves two paths ; one of these is hydrogen ion dependent and other is independent and hydrogen ion concentration. The proposed mechanism is

$$HOOSO_3^- \overset{K}{\rightleftharpoons} \bar{O}-O-SO_3^- + H^+$$

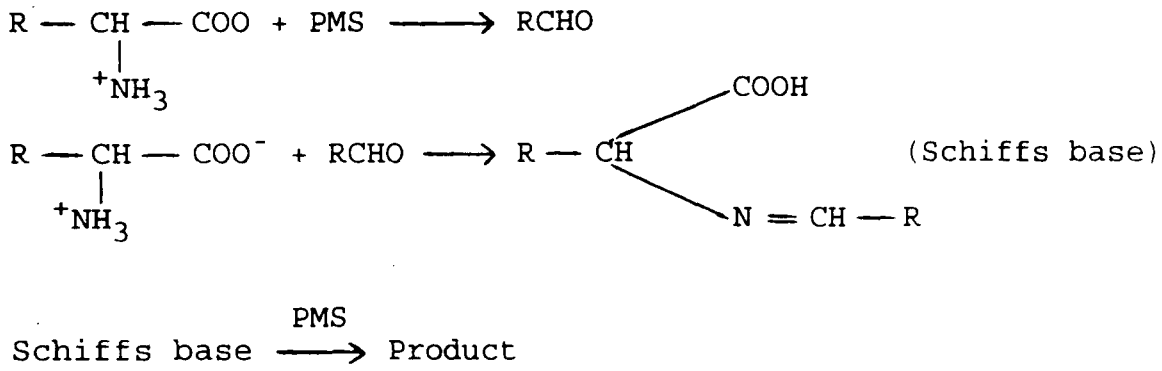
$$\text{Amino acids} + HOOSO_3^- \xrightarrow{k_a} \text{Products}$$

$$\text{Amino acids} + \bar{O}OSO_3^- \xrightarrow{k_b} \text{Products}$$

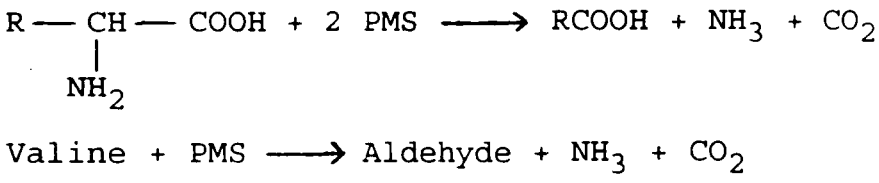
Scheme-I



Scheme - II



Scheme-III



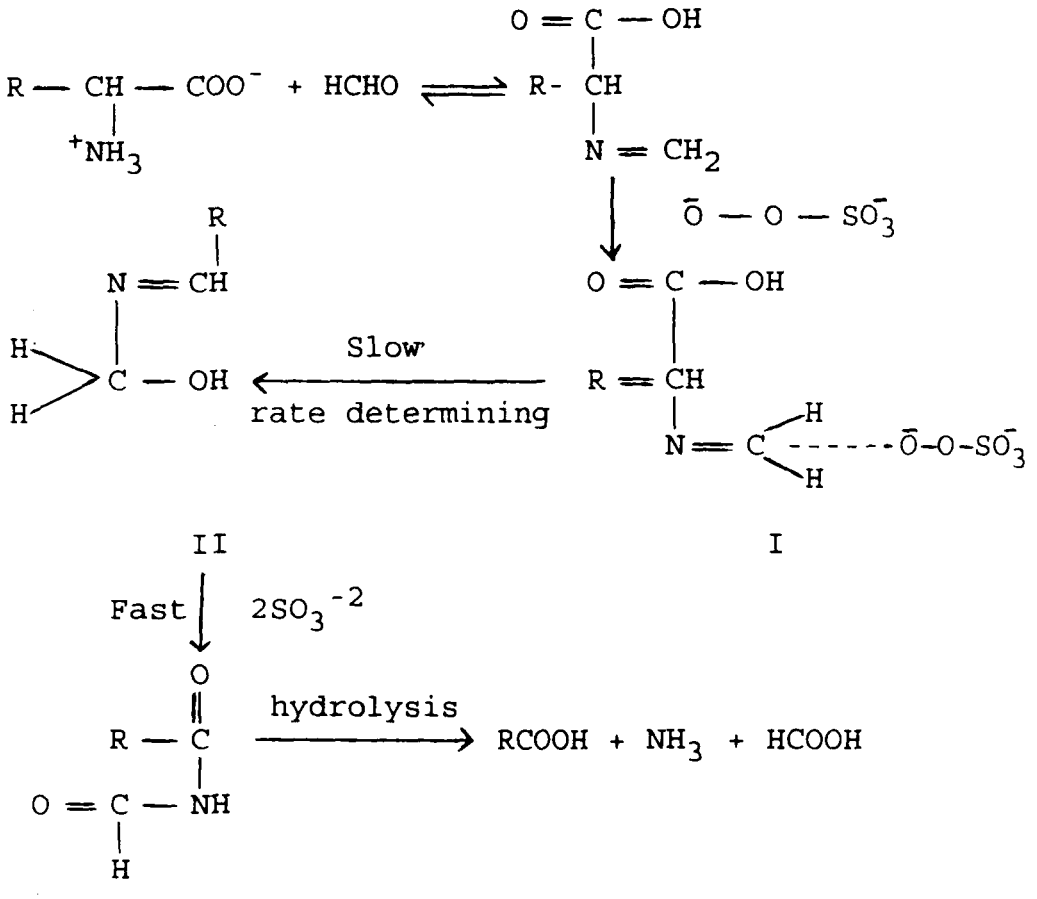
Scheme-IV

The acid-independent and inverse acid dependent paths may be as represented by scheme-I. A nucleophilic substitution mechanism at NH_3^+ group has been proposed. The scheme-III provides the basis for the auto catalyzed effect due to aldehydes initially formed acting with amino acid to give an aldimine (schiffs base) which reacts more readily with PMS.

The kinetics of oxidation of amino acids (S) by peroxomonosulfate (PMS) in the presence of formaldehyde (SH) have been reported by Ramachandran[92] et al. Analysis of the results shows that the rate of oxidation can be represented by,

$$- d[PMS]/dt = k [S] [SH] [PMS] + k'' [SH] [PMS]$$

at constant $[H^+]$. The effect of hydrogen ion concentration on the rate and thermodynamic parameters was also calculated. The kinetic results show the reaction proceed by the formation of a schiffs base as intermediate.

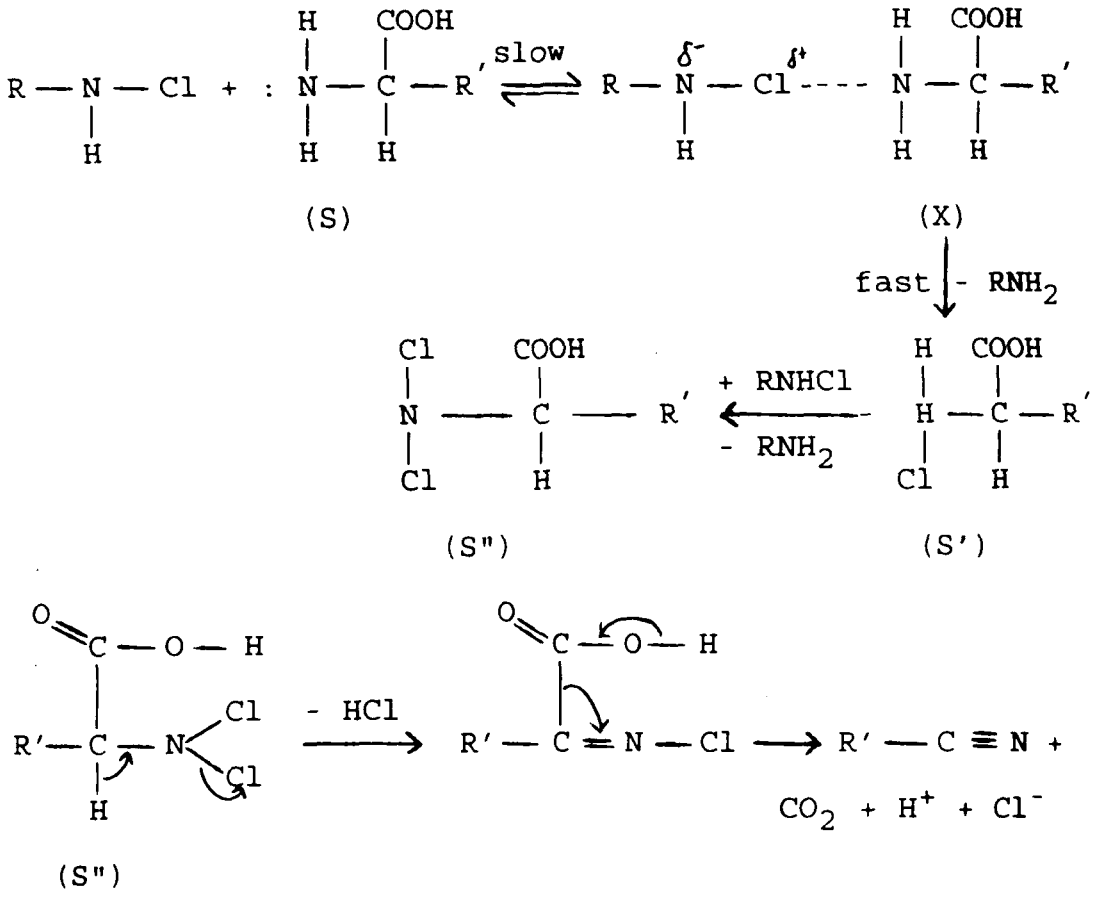


$$R\text{-}CH(NH_2)\text{-}COOH + HCHO + 3\ PMS \longrightarrow RCOOH + CO_2 + NH_3 + HCOOH$$

The authors have suggested a nucleophilic substitution mechanism. On comparing with enzyme-catalyzed decarboxyla-

tion-deamination of amino acids, Ramachandran and his co-workers assumed that the oxidant reacted with $-CH_2$ group of - N - CH_2 to give the activated complex (I) which in the rate-determining step rearranges to give (II) and CO_2. In the oxidation of amino acids by PMS in the presence of aldehyde. Snell[93], has also suggested the reaction of amino acids are normally catalyzed by pyridoxal phosphate-dependent enzymes.

The kinetics and mechanism of oxidation of L-threonine in acid media by sodium N-chloro-p-toluene-sulphonamide (CAT) has been investigated by Gowda[94] et al. at 35°C. They have reported that the reactions follow similar kinetics for a number of amino acids, being first order in [CAT], fractional order in [substrate] and [Cl^-], and of inverse fractional order in [H^+]. Variation of ionic strength and addition of the reaction product, p-toluene sulphonamide, or the ions such as SO_4^{2-} and ClO_4^- had no effect on the reaction rate. The mechanism proposed by Gowda et al. is



(S")

$R = P - CH_3 C_6 H_4 SO_2 -$; $R' = CH_3 CH (OH)^{*}-$

The reaction intermediate (X) formed by the electrophilic attack of RNHCl on the nitrogen of the amino group of threonine (S) undergoes disproportionation to give the mono-N-Chloro derivative of the amino acid (S') which in turn interacts with a second molecule of RNHCl to form the N, N-dichloro derivative (S"). This (S") undergoes molecular rearrangement and subsequent elimination process yield the reaction products. The following is the proposed rate law.

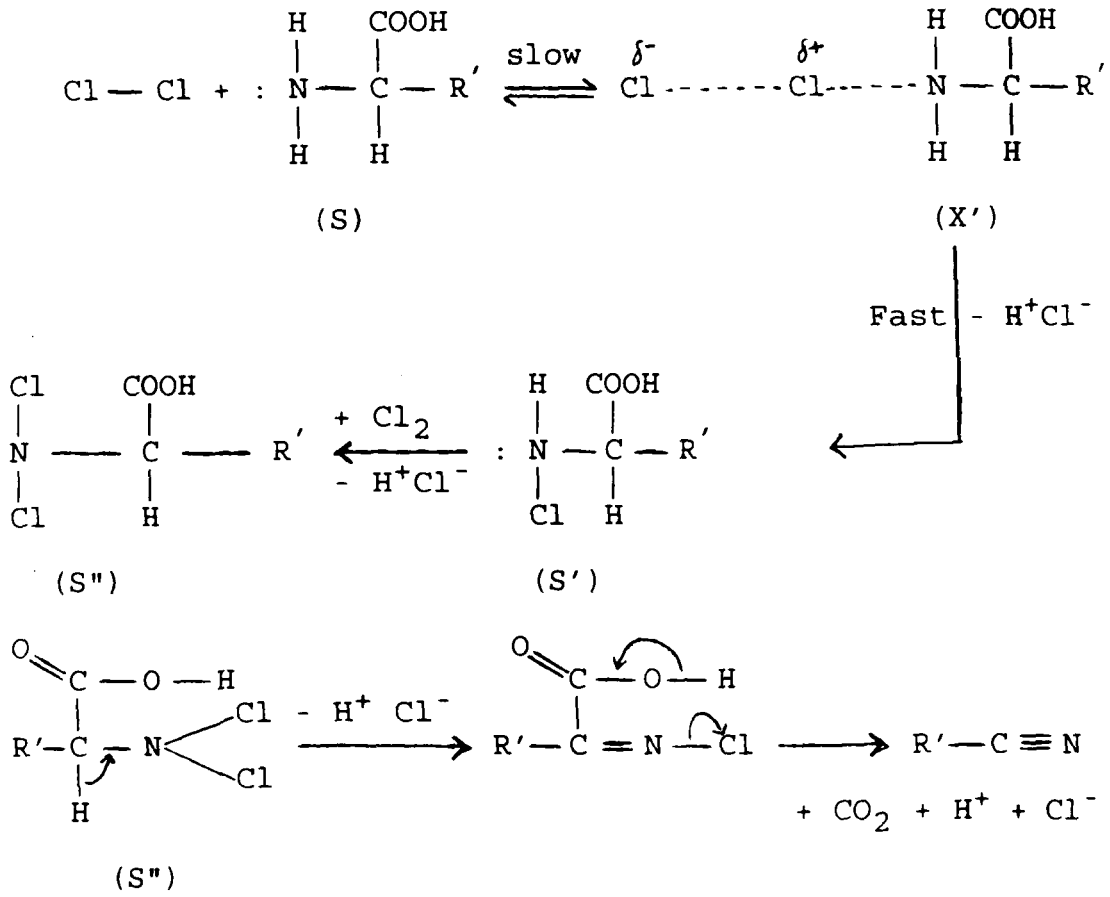
$$- d [CAT]/dt = k_1 k_2 k_3/k_{-1} (k_{-2} + k_3) . [RNHCl][SH^+]/[H^+]$$

$$- d [CAT]/dt = k_6 [RNHCl] [Cl]$$

$$- d [CAT]/dt = k' [RNHCl]$$

The dependence of the observed rate constant, k', on the concentrations of H^+ ion, substrate, and Cl^- ion change, are in excellent agreement as predicted by the above rate law.

Gowda and Mahadevappa[95] have investigated the kinetics and mechanism of oxidations of amino acids by sodium N-chlorotoluene-p-sulphonamide (chloromine-T) in acid and alkaline media. The oxidation in acid medium involves two reactions paths, (a) direct interaction of N-chloro-toluene-p-sulphonamide (RNHCl) with the neutral amino acid in a slow step leading to the formation of the monochloroamino acid which subsequently interacts with another molecule of RNHCl, by a fast step, to give N, N-dichloroamino acid which in turn undergoes molecular rearrangement and elimination to yield the products and (b) the other involves the interaction of Cl_2 or H_2OCl, produced from the disproportionation of RNHCl in the presence or absence of Cl^-, with the substrate to give the products.



$$R'-C\equiv N + Cl-Cl + H_2O \longrightarrow R'CNO + 2H^+ + 2Cl^-$$

In the alkaline medium, however, the presence of a number of species HOCl, $RNCl^-$, and OCl^- makes the kinetic investigation very complicated. They have proposed rate law is in agreement with the observed rate constant.

Gowda and Rao[96,97] have also investigated the kinetics of oxidative decarboxylation of amino acids by CAT in aqueous perchloric acid medium both in the presence and absence of chloride ion. Their investigations show that in the presence of chloride ion the reaction is first

order in $[CAT]_0$. Zero order in $[substrate]_0$ and $[H^+]$ with all the amino acids, however, the kinetic features change completely in the absence of chloride ion. The order with respect to $[CAT]_0$ changes to second order and rate is proportional to [substrate] and inverse first order on $[H^+]$. At low $[H^+]$, the kinetic features are similar those in the absence of chloride. The following mechanism and the rate law have been reported.

$$SH \overset{K_1}{\rightleftharpoons} S + H^+$$

$$S + 2\ RNHCl \xrightarrow{k_2} S' + 2\ RNH_2$$

$$S' \xrightarrow{k_3} Products$$

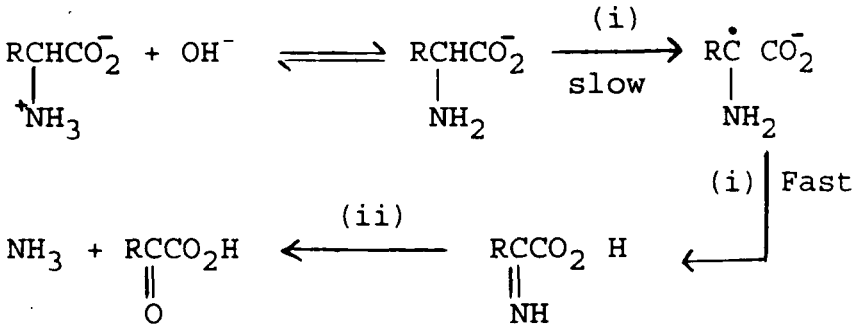
The rate law proposed

$$- d\,[CAT]/dt = k_2\,[CAT]^2\,[S]$$

$$= K_1\,k_2\,[CAT]^2\,[SH]/[H^+]$$

The kinetics of oxidation of amino acids by alkaline hexacyanoferrate (III) have been reported at constant ionic strength over the temperature range 318-338 K by Laloo and Mahanti[98]. The reaction followed Ist order kinetics in substrate and oxidant concentrations, but it was independent of the concentration of the alkali in the range studied. Their observations show that the rate law

dependent on the concentration of the substrate and the oxidant.



Where (i) $[Fe(CN)_6]^{3-}$; (ii) water

The mechanism proposed in a well established pathway for the oxidation of amino acids to keto acid via intermediate formation of amino acid.

Panda and Sahu[99] have studied the kinetics of N-bromoacetamide (NBA) oxidation of amino acids catalyzed by Hg^{++} in the perchloric acid medium, they observed that the reaction is first order in [NBA] and fractional order in [substrate] and $[H^+]$. The proposed reaction mechanism scheme is given below.

$$RCH(\overset{+}{N}H_3)COOH \overset{K_1}{\rightleftharpoons} RCH(NH_2)COOH + H^+$$

$$NBA + H_2O \overset{K_2}{\rightleftharpoons} HOBr + \text{Acetamide (Acm)}$$

$$RCH(NH_2)COOH + HOBr \overset{K_3}{\rightleftharpoons} [\text{complex}]$$

$$[\text{Complex}] \xrightarrow[\text{Slow}]{k_d} RC^+ HNH_2 + CO_2 + H_2OBr$$

$$RC^+ HNH_2 \xrightarrow{-H^+} RCH = NH \xrightarrow{H_2O} RCHO + NH_3$$

Yamuna[100] et al. studied the kinetics of oxidation of α- amino acids by bromamine-T (BAT) in sulfuric acid medium at 35°. The observations show a first order dependence each in $[\text{oxidant}]_0$, $[\text{amino acid}]_0$ and inverse first order in $[H^+]$. Added sulphate ions increases the rate while bisulphate ions retarded the reaction. The rate of oxidation increases in the order : leucine > alanine > serine > glycine. The mechanism assumes that the interactions of zwritterion of substrate with monobromamine-T is not involved in the rate limiting step. Furthermore, it has been observed that ionic strength of the medium has no effect on the rate, suggesting that neutral species are involved in the rate determining step. The following proposed mechanism accounts for the observed kinetics :

$$SH^+ \underset{}{\overset{K_1}{\rightleftharpoons}} S^\circ + H^+$$

$$S^\circ + RNHBr \xrightarrow[\text{slow}]{k_2} X$$

$$X + n\ RNHBr \xrightarrow{k_3} \text{Products}$$

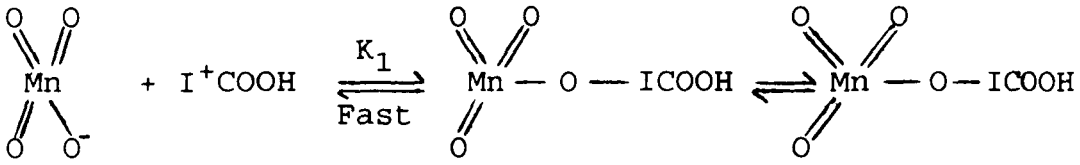
Ramachandran and Vivekanandam[101] have investigated the oxidation of amino acids in aqueous medium. The results indicate that the rate of oxidation follow second order kinetics with respect to chloramine-T [CAT] and inverse dependence on [P-toluenesulfonamide]. At constant $[RNH_2]$ the rate expression of the reaction is

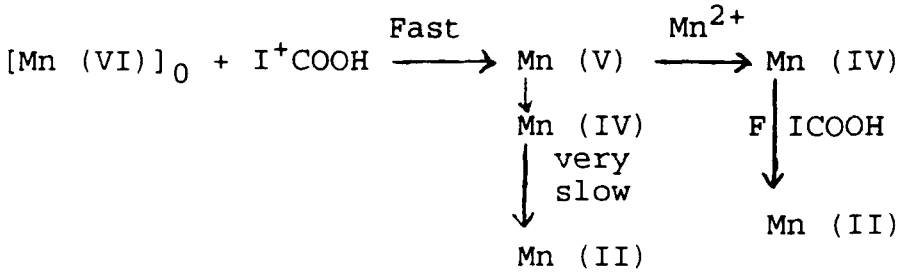
$$- d[CAT]/dt = k_a [CAT]^2 + k_b [\text{Amino acid}] [CAT]^2/[H^+] + k_c [\text{Amino acid}] [CAT]^2/[H^+]^2$$

A linear relationship between pk_1 and the rate constants shows the electrophilic attack of the oxidant at the carboxylate group of amino acid. The mechanism of the reaction has been discussed in terms of the observed kinetic data.

The kinetics and mechanism of oxidation of isoleucine by acid permanganate was studied by Hussain and Ahmad[102]. The results reported show that the plot between A^{525} (observed absorbance at 525 nm) Vs. time increases initially at low concentration of isoleucine, for significant duration, it is suggested that the formation of Mn (IV) as intermediate is taking place simultaneously along with Mn (III) produced by the same transient species of Mn (VII). In one of the paths, it appears that the transient species is reacting with amino acid leading to

the formation of Mn (IV) only. Thus the fate of Mn (VII) during the course of reaction may be represented as





The over all rate expression of the reaction is

$$\frac{-\,d\,[Mn\ (VII)]_{total}}{dt} = \frac{k\,[ICOOH]_0}{a+b\,[H^+] + C\,[ICOOH]}\,[Mn\ (VII)]_{total}$$

The kinetics of oxidative degradation of leucine[103] (LCO_2H) has been followed spectrophotometrically at 525 nm for the disappearance of Mn (VII) and at 420 nm for the appearance of Mn (IV). The results signify that the reaction is first order with respect to $[MnO_4^-]$. The rate constant k_7 for the disappearance of Mn (VII) has been evaluated at different $[LCO_2H]$ and $[H^+]$ and at different temperatures from the plot of A^{525} Vs time. The over all rate satisfying the kinetics parameters is

$$-\frac{1.d\ [Mn\ (VII)]_{total}}{[Mn\ (VII)]_{total}\ dt} = \left\{\frac{[k'\ [LCO_2H]_o^{1/2} + k'_2\ [LCO_2H]_o^2}{[H^+]}\right\}$$

It is also reported that the decarboxylation involved a cyclic chain reaction.

The oxidation of serine by acid permanganate was also investigated by the same authors[104] both in the presence and absence of SDS. It has been shown that the presence of surfactant enhance the reaction rate. The reaction is first order with respect to [Serine] and $[MnO_4^-]$, the reaction is retarded by $[H^+]$ in the absence of SDS but catalyzed in the presence of SDS. The overall rate expression for the reduction of Mn (VII) is given as

$$-\frac{d\ [Mn\ (VII)\ total}{dt} = \{[k'_{4f}+k'_{2f}/[H^+]\}[Serine]_0[Mn(VII)]_{total}$$

and in the presence of SDS,

$$-\frac{d\ [Mn(VII)]_{total}}{dt} = \{k[H^+]+k'\}\ [Serine]_0\ [SDS]\ [Mn(VII)]_{total}$$

Where k'_{4f} and k'_{2f} are rate constants of reaction path leading to the formation of Mn(VI) and Mn(II) respectively. The reaction appears to involve a parallel consecutive reaction mechanism.

The stopped flow[105] technique was used to study the kinetics and mechanism of the oxidation of tryptophane (WCOOH) by acid permanganate in the absence and presence of SDS. The results signify that the reaction is first order with respect to $[MnO_4^-]$ and a fraction order in [WCOOH]. However, in the presence of SDS the reaction is first order with respect to $[MnO_4^-]$ and [WCOOH]. The reaction is accelerated by increase in the concentration of hydrogen ion, both in the absence and presence of SDS. The overall rate expression for the reduction of manganese (VII) by tryptophane is given as :

$$-\frac{d\,[Mn(VII)]_{total}}{dt} = \frac{k_1\,[WCOOH]_0[H^+]}{K' + K\,[H^+] + k_2\,[WCOOH]}\,[Mn\,(VII)]_{total}$$

and in the presence of SDS

$$-\frac{d\,[Mn\,(VII)]_{total}}{dt} = Kk'_2\,[WCOOH]_0\,[H^+][SDS][Mn(VII)]_{total}$$

Srivastava[106] et al. have reported that the oxidation of amino acids by cerium (IV) in nitric acid solution is first order each in [Ce (IV)] and [amino acid]. The reaction rate increases linearly with increase [Ag (I)] and $[HNO_3]$. Added potassium nitrate retards the reaction rate. A suitable reaction mechanism has been suggested.

$$Ag^{+} + A—A \overset{K}{\rightleftharpoons} [Ag^{I}—A—A]$$

$$[Ce\ (OH)]^{3+} + H^{+} \overset{K'}{\rightleftharpoons} Ce^{4+} + H_2O$$

$$[Ag^{I}—A—A] + Ce^{4+} \xrightarrow{k_1} [Ag^{II}—A—A] + Ce^{3+}$$

$$[Ag^{II}—A—A] \xrightarrow{k_2} Ag^{+} + H^{+} + R—CH(NH_2)\ COOH$$

$$R—CH(NH_2)\ COOH \longrightarrow \text{Products}$$

Kinetics of oxidation of aspartic acid by chloramaine-T in aqueous sodium hydroxide medium in the presence and absence of Hg^{II} has been investigated by Satish and Yadav[107]. A first order dependence on chloromine-T and aspartic acid concentrations both in absence and presence of Hg^{II} has been observed. Inverse first order dependence on sodium hydroxide concentration has been established for both uncatalyzed and catalyzed oxidation of aspartic acid. Hg^{II} ions catalysis the reaction significantly and the catalytic action of Hg^{II} is ascribed to the complex formation with aspartic acid anions.

The kinetics of oxidative decarboxylation of amino acids by bromamine-T (BAT) has been studied in alkaline medium at 293 K by Gowda and Rao[108]. The rate followed first order kinetics in [oxidant], zero order in [amino

acid] and fractional order in [OH^-]. The rate increased with an increase in ionic strength of the medium. Addition of the reduced product of oxidant (p-toluenesulphonamide) decreased the rate. The oxidation process has been shown to proceed by two path way mechanism.

$$RNBr^- + H_2O \xrightarrow[\text{slow}]{k_1} RNH^- + HOBr$$

$$HOBr + R'CH(NH_2)COO^- \xrightarrow[\text{fast}]{k_2} R'CH(NH_2)COOBr + OH^-$$

$$R'CH(NH_2)COOBr \xrightarrow[\text{fast}]{k_3} R'CH(NH) + CO_2 + H^+Br^-$$

$$R'CH(NH) + H_2O \xrightarrow[\text{fast}]{k_4} R'CHO + NH_3$$

$$RNH^- + H_2O \xrightarrow[\text{fast}]{k_5} RNH_2 + OH^-$$

The corresponding rate law is

$$-d[BAT]/dt = k_1[BAT][H_2O]$$

$$RNBr^- + OH \xrightarrow[\text{slow, rds}]{k_6} OBr^- + RNH_2$$

$$OBr + H_2O \xrightarrow[\text{fast}]{k_7} HOBr + OH^-$$

$$HOBr + R'CH(NH_2)COO^- \xrightarrow[\text{fast}]{k_8} R'CH(NH_2)COOBr + OH^-$$

$$R'CH(NH_2)COOBr + H_2O \xrightarrow[\text{fast}]{k_9} \text{Products}$$

$$RNH^- + H_2O \xrightarrow{k_{10}} RNH_2 + OH^-$$

The related rate law is

$$-d[BAT]/dt = k_6[BAT][OH^-]$$

De Andres[109] et al. have studied the kinetics of oxidation of L-alanine by permagnate ion in phosphate buffers. The reaction autocatalyzed by the product identified as a soluble form of colloidal manganese dioxide which is stabilized in solution by absorption of phosphate ion on its surface. The rate of the non-catalytic reaction pathway is first order in both the oxidizing and reducing agents, and increases with the pH of the medium. The rate of the catalytic reaction pathway is first order in both the oxidizing and autocatalytic agents. The reaction follows the Freundlich adsorption isotherm as far as reducing agent concentration is concerned, and increases with the pH of the medium. The proposed mechanism is

$$CH_3CH(\overset{+}{N}H_3)CO_2^- + MnO_4^- \xrightarrow{\text{slow}} CH_3CH(^+NH_3)\dot{C}O_2 + MnO_4^{2-}$$

$$CH_3CH(\overset{+}{N}H_3)\dot{C}O_2 \longrightarrow CH_3\dot{C}H(^+NH_3) + CO_2$$

$$CH_3\dot{C}H\,\overset{+}{N}H_3 \longrightarrow CH_3\dot{C}HNH_2 + H^+$$

$$CH_3\dot{C}HNH_3 + MnO_4^- \longrightarrow CH_3CH = {}^+NH_3 + MnO_4^{2-}$$

$$CH_3CH = {}^+NH_2 + H_2O \longrightarrow CH_3CHO + NH_4^+$$

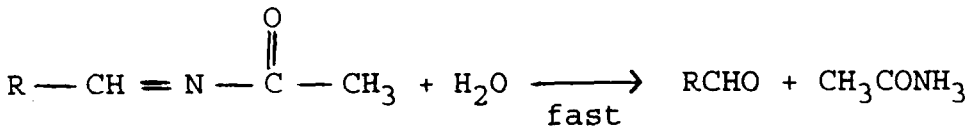
$$3\ MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^- + 4OH^-$$

The kinetic of oxidation of amino acids by N-bromoacetamide in alkaline medium have been studied by Reddy[110] et al. The amino acids are oxidized to the corresponding aldehydes, ammonia and carbon dioxide. The effect of varying [substrate], [oxidant], [OH^-] and ionic strength have been studied. The reaction is first order in [NBA] and fractional order each in [substrate] and [OH^-]. Addition of acetamide does not effect the rate of oxidation. Thermodynamic parameters have been calculated and a suitable mechanism is

$$CH_3CONHBr + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} CH_3C\bar{O}NBr + H_2O$$

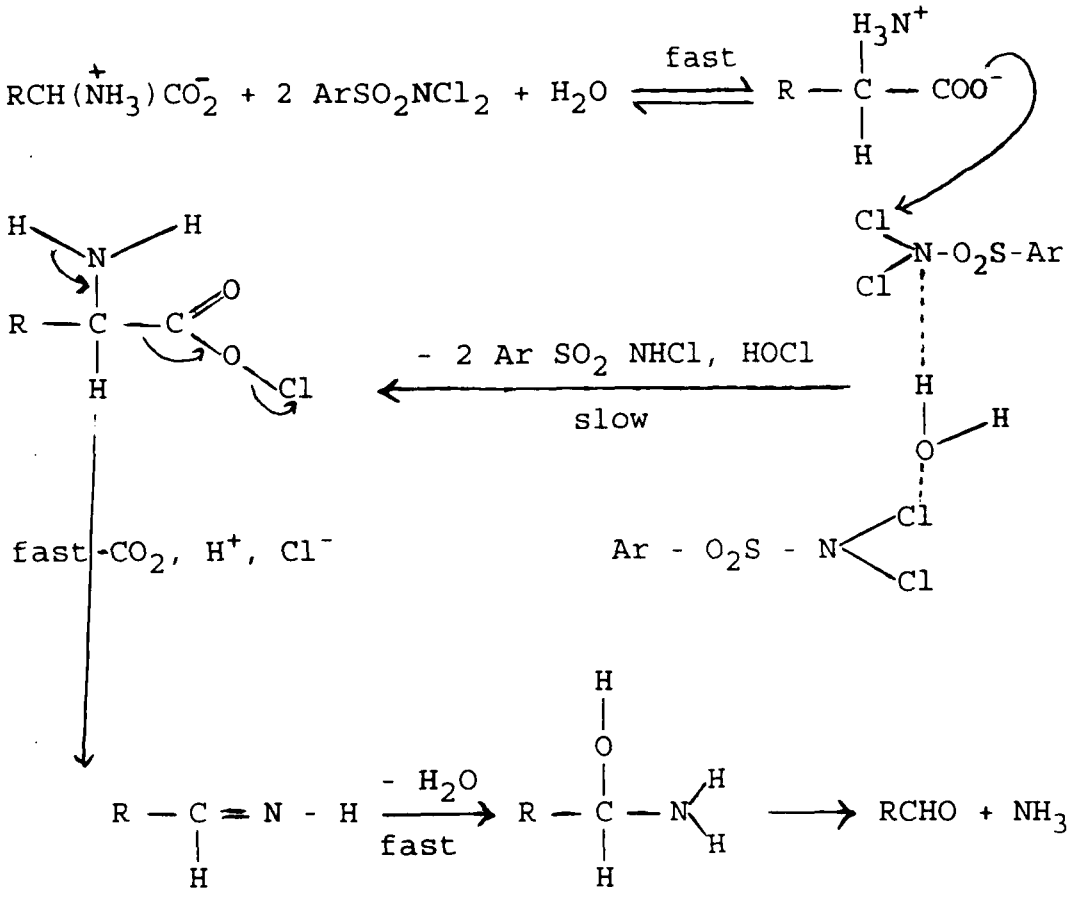
$$RCH(NH_3)^+ COO^- + CH_3CONBr \overset{K_2}{\rightleftharpoons} \left[\begin{array}{l} \overset{NH_3^+}{\vdots} \\ R - \overset{\vdots}{CH} - COO^- \\ \overset{\vdots}{N} - Br \\ | \\ CH_3 - C = O \end{array} \right]$$

$$\left[\begin{array}{l} \overset{NH_3^+}{\vdots} \\ R - \overset{\vdots}{CH} - COO^- \\ \overset{\vdots}{N} - Br \\ | \\ CH_3 - C = O \end{array} \right] \xrightarrow[\text{slow}]{k_d} R - CH = N - \overset{O}{\overset{\|}{C}} - CH_3 + NH_3 + CO_2 + Br^-$$



The proposed mechanism involves the formation of a complex between NBA^- and zwitterionic form of the amino acid followed by the decomposition of this complex in a slow step.

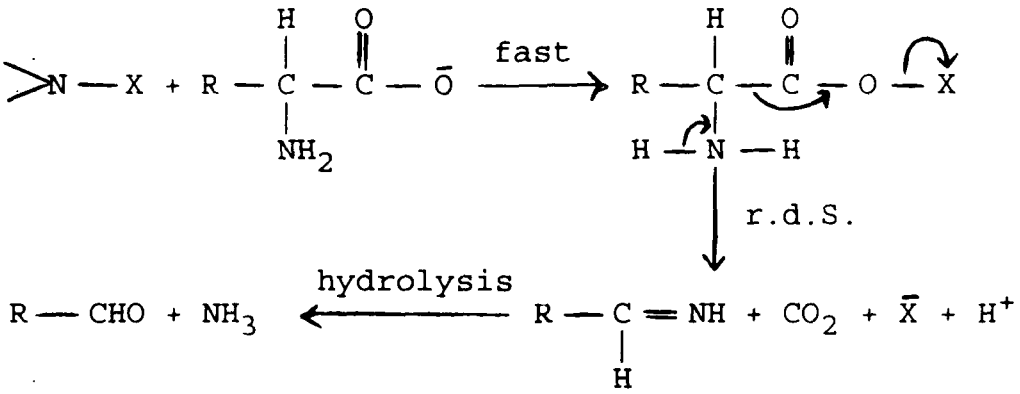
Gowda and Rao[111] have studied the kinetics and mechanism of oxidation of several amino acids by N, N-dichloro-p-toluenesulfonamide (generally known as dichloramine-T) via 1:1 (v/v) water methanol medium in the presence of perchloric acid. The oxidation of alanine and leucine showed second order kinetic in [oxidant], first order in [amino acids] and inverse fractional order in $[H]^+$ over the entire range of $[HClO_4]$ (0.005-0.10 $moldm^{-3}$) used. But the kinetics of oxidations of aspargine, glutamine and proline were $[H^+]$ dependent. The rate dependence in [oxidant] was second and first orders in $[H^+]$ ranges 0.0005-0.005 $moldm^{-3}$ and 0.005-0.10 $moldm^{-3}$, respectively. The kinetic in [amino acid] for these oxidations were also different, variation of ionic strength of the medium or addition of the reduced product of the oxidant had no or negligible effects on the rates of reactions. A mechanism suitable with the observed kinetics is proposed.



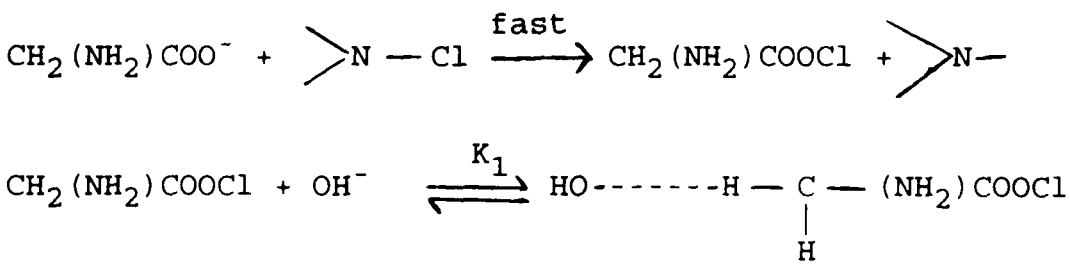
Where, R = CH_3 (Ala), $(CH_3)_2$ $CHCH_2$ (Leu), $H_2N(CO)CH_2$(Asn) and $H_2N(CO)CH_2CH_2$ (Gln)

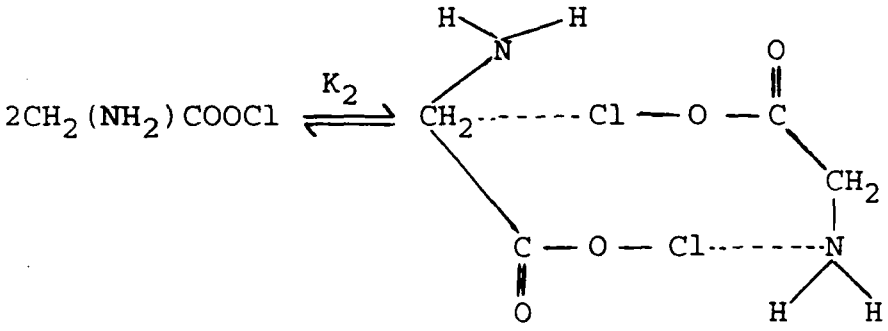
Ramachandran[112] et al. have studied the kinetics of oxidation of a dozen of α - amino acids (AA) by N-chloro-succinimide (NClS) in aqueous alkaline media. They compared the results with those of N-bromosuccinimide (NBS) oxidation. The observed rate of oxidation is first order in [oxidant] and zero-order in [substrate]. The rate of oxidation increases with increase in $[OH^-]_{free}$ in

[NClS] with the exception of amino acids having β -alkyl substituent such as valine, leucine etc. Perusal of results show that NClS/NBS reacts with -amino acid anion to produce α-amino acyl hypohalite which then decomposes in the rate-determining step to give the products. The intermediate α-amino acyl hypohalite is identified by UV-visible absorption spectra. Glycine behaves differently from other amino acids in both oxidants. The proposed mechanism is consistent with the observed kinetics.

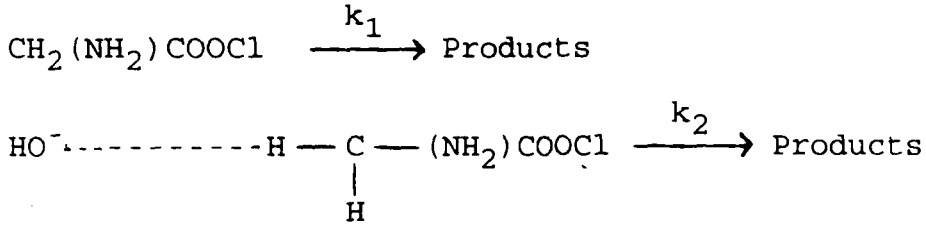


In the case of Glycine :





Dimer



Based on the experimental observations a reaction scheme involve the decomposition of the intermediate, ∝-amino acyl hypohalite has been proposed.

The kinetics of the oxidation of L-leucine[113] by chloramine- T in the presence of cationic surfactant [i.e. cetyltrimethyl ammonium bromide, (CTAB)] were studied at 30°. The rate constants increased initially and then decreased with an increasing concentration of CTAB. The micelle substrate binding constant has been calculated. The effects of halide ions, solvents, and ionic strength on the reaction rate were also studied at different temperatures and values of activation parameters were calculated.

Alvarez[114] studied the oxidation of amino acids with Cr(IV) in perchloric acid medium, the reaction was followed spectroscopically, showing first order kinetics each in Cr(IV) and substrate concentrations. The dependence of reaction rate on hydrogen ion concentration show a complex behaviour.

The kinetics of oxidation of amino acids by 1-chlorobenzotriazole (CBT) was studied in $HClO_4$ at 283 K by Mayanna and Channegowda[115]. The reaction followed first order kinetics in [CBT] and fractional order in amino acid concentration. Hydrogen ions retarded the reaction showing inverse fractional order. The solvent isotope effect was also studied, however, variation of ionic strength, addition of reaction product and of dielectric constant had no effect on the rate.

Kinetics of oxidation of amino acids by hexachloroiridate (IV) (HCI) in aqueous acid medium at pH range of 2.5-3.5 by Kumar[116] et al. The observed rate is pseudo-first order in [Ir(IV)] in the presence of excess substrate. The rate increases with increase in [substrate] and the order in [Ir(IV)] is fractional. The rate also increases with increase in $[H^+]$.

The following mechanism has been proposed.

$$\underset{[AA]}{H_3\overset{+}{N}\text{-}CH(R)\text{—}COO^-} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{[AAH^+]}{H_3\overset{+}{N}CH(R)COOH}$$

$$AAH + Ir\ (IV) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{complex (C)}$$

$$C \xrightarrow{k_3} \text{free radical} + Ir\ (III)$$

$$\text{Free radical} + Ir(IV) \xrightarrow[\text{fast}]{} \text{Product} + Ir(III)$$

The formation of free radicals by the transfer of electron from substrate to oxidant is assumed to be rate determining step.

The kinetic of oxidation of valine by chloramine-T in the presence of sodium dodecyl sulfate at 40° is first order in oxidant and fractional order in valine as reported by Nagar[117] et al. The graph of the rate constant versus [detergent] is parabolic and the value of positive cooperativity is 1.83 showing interaction between micelle and substrate.

In HCO_3^-/CO_2 buffer, the oxidation of amino acids by H_2O_2 is catalyzed by Mn(II) and Fe(II) and the amino acid-facilitated dismutation of compounds per mol of leucine[118] oxidized was essentially constant. In the absence of Fe(II), the rate of Mn(II)-catalyzed leucine oxidation was directly proportional to the H_2O_2, Mn(II), and amino acid concentration, and was proportional to the square of HCO_3 concentration. The rate of Mn(II) catalyzed O_2 production in the presence of 50 mM alanine or leucine was $\sim$4 fold the rate observed in the absence of amino acids and

accounted for 50% of the H_2O_2 consumed; the other 50% of the H_2O_2 was consumed in the oxidation of amino acid. The O_2 production was increased nearly 18 fold in the presence of α-methylalanine and accounted for $\sim$ 90% of H_2O_2 decomposition is an inner sphere (cage-like) process catalyzed by a Mn coordination complex of the compounds, Mn(II), amino acid, $(HCO_3^-)_2$. The oxidation of amino acid in this complex most likely proceeds by a free radical mechanism involving H abstraction from the -c as a critical step. The result demonstrated that at physiological concentration of HCO_3^- and CO_2, Mn(II) is able to facilitate Fenton-type reactions.

Radhkrishnamuriti and Panigrahi[119] have studied the kinetics of oxidation of some α-amino acids by trichloromelamine (TCM) in aqueous acetic acid-sodium acetate buffer system. The reaction follows a first order kinetics in the disappearance of TCM and a fractional order in [amino acid]. The pseudo-first order rate constant increases with the increasing pH of the medium. Salts like $NaClO_4$ and KI have no effect on the reaction rate but addition of melamine enhances the rate constants (k_D) for individual substrates which have been determined at 30°, 35° and 40° and used for the evaluation of activation parameters and to establish correlation of the structure reactivity.

The kinetic investigation of the oxidation of monoaminomonocarboxylic acids (i.e. glycine and alanine) by chloromine-T (CAT) have been made by Nagar[120] et al. in the presence of cetyl trimethylammonium bromide (CTAB) in the acidic medium. The rate shows a first order dependence on [oxidant] but is fractional in case of the substrate concentration. Whereas, $[Hg^{+2}]$ shows a positive effect on reaction rate but ionic strength and presence of the added halide ions have no effect. The reaction mechanism and rate laws on the basis of experimental results, are proposed as under :

(i) In the absence of surfactant

$$-\frac{d[CAT]}{dt} = \frac{kWK[CAT][S]}{1+k[S]}$$

(ii) In the presence of surfactant

$$nD \rightleftharpoons Dn$$

$$Dn + S \rightleftharpoons S.Dn$$

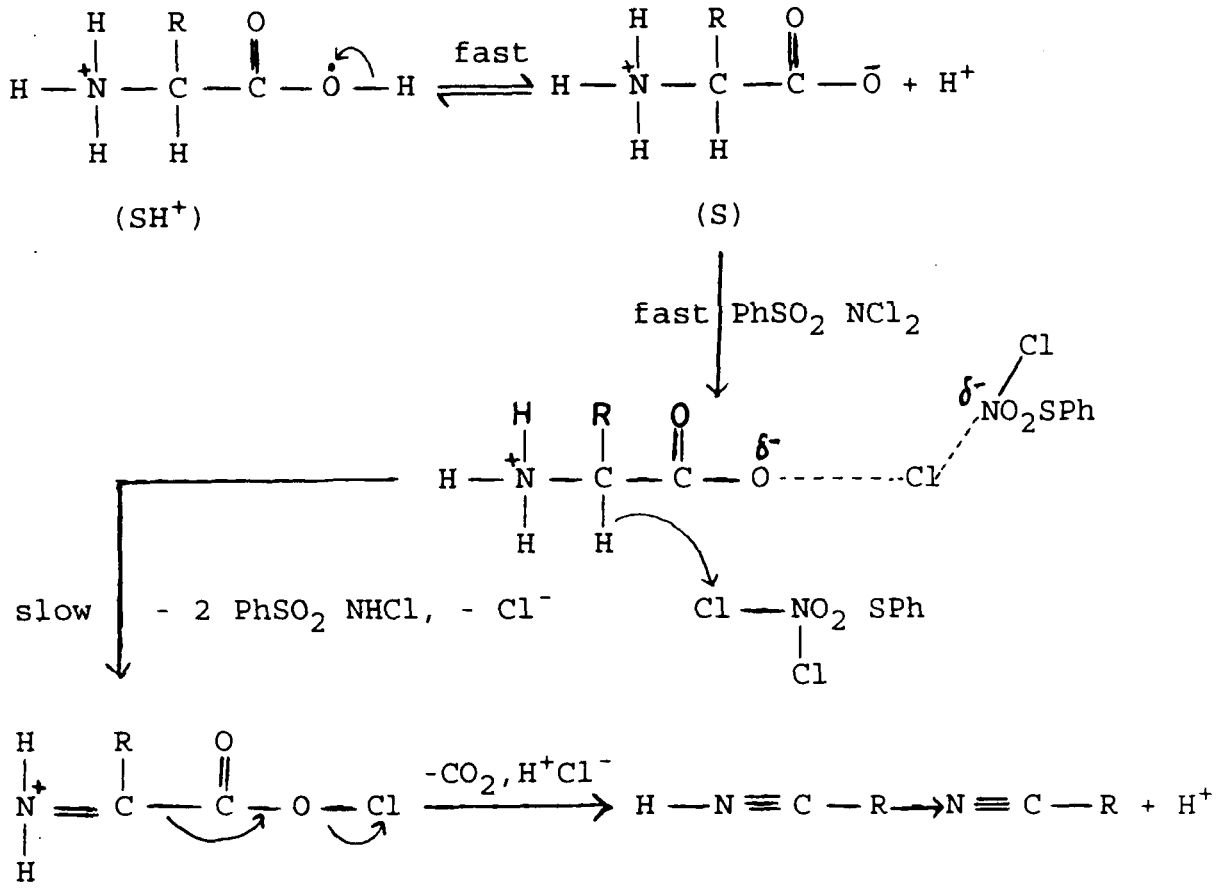
$$S.Dn + CAT \xrightarrow{slow} Dn + H^{+} + CH_3C_6H_4SO_2NH_2 + CO_2 + NaCl + Product$$

Where, Dn is the most abundant micellar species with aggregation number n. Observed rate is given as :

$$k_{obs} = \frac{kW + kS\ KD\ [Dn]}{1 + kD\ [Dn]}$$

Increasing the concentration of surfactant increases the rate constants sigmodally to a plateau beyond which there is no more enhancement in the rate. This behaviour is attributed to substrate-destabilisation-stabilisation in the polar environment of the aggregates. The association molecule is governed by hydrophobic and electrostatic interactions. The longer hydrocarbon chain in amino acid, the greater is the extent of its incorporation in a cationic micelle.

Rao and Gowda[121] have investigated the kinetics of oxidation of glycine, alanine, valine, leucine, and phenylalanine by dichloramine-B (DCB) in a mixed reaction medium of aqueous methanol (1:1, v/v) in the presence of perchloric acid. At low concentration of $HClO_4$ (0.0005-0.005 $mold^3$), the reaction is second order in [DCB], fractional order in [AA] and inverse fractional order in $[H^+]$. In higher concentration range where $HClO_4$ > 0.005 the reaction rate shows a change in its dependence on amino acid concentration. From fraction order it changes to first order in [AA]. However, the pattern in respect of concentrations of DCB and hydrogen ion remains same. The reaction increases slightly with increasing ionic strength of the medium, and decreases with increase in methanol composition of the solvent. In confirmity with the observed kinetic features the following reaction mechanism has been proposed.



Karim and Mahanti[122] studied the kinetics of oxidation of amino acids by quinolinium dichromate in acid medium at constant ionic strength. The reaction was found to be first order in [substrate], [oxidant] and $[H^+]$. Under the cationic form amino acids has been identified as the reactive species. The kinetic isotope effect indicated that cleavage of the carbon-hydrogen bond in the rate determining step was not involved.

Suryanoryana and Raman[123] have studied the kinetics of OsO_4 catalyzed oxidation of amino acids by chloramine-T

in alkaline medium. The oxidation rate shows first order behaviour, however, decreases with increase in pH. Thus observed rate constant consisted of two terms, represented as $k_{obs} = k_{unCAT} + k_{CAT}$. The kinetic results suggest a mechanism involving the formation of an adduct between Os (VIII) and amino acid. The oxidation product is a nitrile.

Palladium (II) has been used as catalyst[124] in the kinetic studies of oxidation of amino acids (glycine, alanine and valine) by N-bromo succinimide (NBS) in perchloric acid medium. The reaction exhibits a first order rate dependence with respect to [NBS]. With respect to substrate concentration the order undergoes a change from first to fractional order in the presence of the catalyst. However, with increasing [hydrogen ion] a retarding effect on the oxidation rate is observed in each case. The rate expression includes a term proportional to $\{k' + k'' [PdCl_2]\}$, where k′ and k" are rate constants for uncatalyzed and catalyzed paths, respectively.

The kinetics of the Ag (I) catalyzed oxidation of L-glutamic acid with peroxodiphosphate (PdP) in acetate buffer medium has been studied by Mishra[125] et al. The rate is independent of hydrogen ion concentration. The overall rate law is,

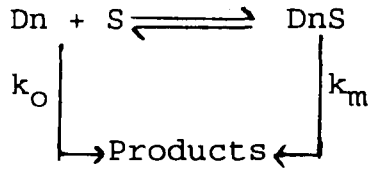
$$-\frac{d[Glu]}{dt} = \frac{k_1 k_3 K [PdP][Glu][Ag\ (I)]}{(k_2 + k_2)\ (1+K[Glu])}$$

k_s involved in the above rate expression have been calculated at three temperatures.

Satyanorayana[126] et al. have investigated the kinetics of oxidation of amino acids in aqueous-acetic acid medium at different perchloric acid concentration by trichloroisocyanuric acid, (TClCA). The reaction is first order in TClCA, inverse first order in $[H^+]$, with the exception of DL-isoleucine and DL-Aspartic acid for other amino acid the reaction is zero order. Increase in the proportion of acetic acid in solvent medium retards the rate. The σ^* is found to be 0.54 and the order of reactivity is DL-aspartic acid > L-glutamic acid > L-histidine > DL-valine > DL-isoleucine > DL-alanine > glycine.

Recently, Vibha Nagar[127] et al. have studied the kinetics of oxidation of amino acids by chloromine-T in the presence of two different surfactants (CTAB and SDS) in acidic medium. The kinetic results suggest that the reaction is fractional in substrate concentration and first order with respect to oxidant concentration. The rate is unaffected by an increase in the ionic strength and halide ion concentration. The effect of surfactants on

the reaction has been used to evaluate the micelle-substrate binding constant (K) and co-operativity index indicating the stability of catalyst substrate micelle (complex) so formed. A probable reaction path has been suggested:



Where k_o and k_m are rate constants in absence and presence of surfactant aggregates.

Where concentration of micelles Dn is given by

$[Dn] = (C_D - cmc)/N$

with C_D is stoichiometric concentration of the detergent, N is the aggregation number of the micelle.

$$\frac{k_{obs} - k_o}{k_m - k_{obs}} = K (C_D - cmc)/N$$

The kinetics of oxidation of cysteine and proline by hexacyanoferrate (III) and permanganate, respectively has been studied in basic medium at 25° by Abdel-Halim and Yasmeen[128]. The reaction rate was measured, spectrophotometrically, in alkaline medium. Results showed the rate of oxidation of cysteine is zero order for the alkali, first order for the oxidant, substrate

concentrations and fractional order for the [proline] with permanganate. The value of the rate constant for cysteine-hexacyanoferrate (III) oxidation is two fold of magnitude larger than that for proline-permanganate oxidation.

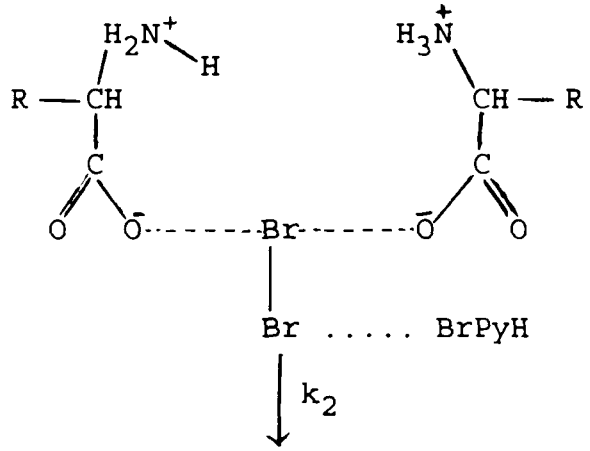
The kinetics of oxidation of amino acids with Cr (VI) in aqueous perchloric acid medium has been studied spectrophotometrically by Alvarez-Macho[129]. The reaction follows second order kinetics at a given concentration of perchloric acid. It is reported that the rate is related to the acidity function and also to the concentration of acid. Primary salt effect was also investigated.

Banerji[130] et al. have studied the kinetics of oxidation of nine α-amino acids by pyridinium hydrobromide perbromide (PHPB) in aqueous acetic acid leading to the formation of the corresponding aldehydes. The reaction is first order with respect to PHPB. Michaelies-Menten type kinetics are observed with respect to some of the amino acids while other amino acids exhibit over-all a second order dependence. The importance of the cleavage of the α-C-H bond in the rate determining step, has been proved by kinetic investigation of isotope effect. The effect of solvent composition indicates that the reaction rate increases with an increase in the polarity of the medium. Pyridinium hydrobromide and bromide ion have no

effect on the rate of oxidation. The reaction is susceptible to both polar and steric effect of substituents. The oxidation of amino acid by PHPB in the atmosphere of nitrogen failed to induce polymerisation of acrylonitrile, showing lack of free radical formation.

$$2\ RCH(^{+}NH_3)\ COO^{-} + Py\ H^{+}\ Br^{3-}$$

$$\rightleftharpoons K$$



$$\downarrow k_2$$

$$RCH = {}^{+}NH_2 + CO_2 + Br^{-} + HBr + PyHBr + RCH\ (\overset{+}{N}H_3)COO^{-}$$

$$RCH = {}^{+}NH_2 + H_2O \xrightarrow{\text{fast}} RCHO + NH_4^{+}$$

The kinetics and mechanism of oxidation of several amino acids by less common oxidants have also appeared in the literature which have been included in tabular form,[131-155] by debaromyces kloecker[156], by phenylisothioicy-anate[157], photo oxidation of amino acid by chlorophyll[158] with alkaline bromine[159].

TABLE : OXIDATION OF AMINO ACIDS

S.No.	Amino acids	Oxidant	Medium	Products	Rate Law	Ref.
1.	Arginine, threonine and glutamic acid	1-chloro-benzotriazole	$HClO_4$	nitrile, carbon-dioxide	$-\frac{d[CBT]}{dt} = k_2[C][SH]$	89
2.	Glycine, alanine, butyrine, valine, leucine and norleucine	peroxomono-sulfate (in the absence of formaldehyde)	acid medium	aldehyde, ammonia & carbondioxide	$-\frac{d[PMS]}{dt} = k_a[\text{amino acid}][HSO_5] + k_b K[\text{amino acid}]\frac{[HSO_5]}{[H^+]}$ $-\frac{d[PMS]}{dt} = k[S][SH][PMS] + k''[SH][PMS]$	91, 92
3.	Threonine	chloramine-T	HCl, $HClO_4$ H_2SO_4	nitrile, amine & carbondioxide	$-\frac{d[CAT]}{dt} = \frac{k_1k_2k_3}{k_{-1}(k_{-2}+k_3)}\frac{[RNHCl][SH]}{[H^+]}$	94
4.	Alanine, phenylalanine, leucine, glutamine, glutamic acid, serine, glycine, histidine, arginine, threonine, glycind and valine	chloramine-T	HCl, $HClO_4$ H_2SO_4	nitrile, amine & carbondioxide	$-\frac{d[CAT]}{dt} = k''[CAT][S][H^+]$	95
5.	Alanine, valine and phenylalanine	chloramine-T	perchloric acid medium	nitrile, amine & carbondioxide	$-\frac{d[CAT]}{dt} = \frac{K_1k_2[CAT]^2[SH^+]}{[H^+]}$	97
6.	Glycine, serine, alanine and leucine	bromamine-T	sulfuric acid medium	nitrile, amine & carbondioxide	$-\frac{d[BAT]}{dt} = \frac{K_1k_2[SH^+][RNHBr]}{[H^+]}$	100

S.No.	Amino acids	Oxidant	Medium	Products	Rate Law	Ref.
7.	Isoleucine	acid per-manganate	perchloric acid medium	ammonia, carbon-dioxide & alde-hyde	$-\frac{d[Mn(VII)]_{total}}{dt} = \frac{k[ICOOH]_0}{a+b[H^+]+c[ICOOH]}[Mn(VII)]_{total}$	102
8.	Leucine	acid per-manganate	perchloric acid medium	aldehyde, ammonia & carbondioxide	$-\frac{1}{[Mn(VII)]_{total}}\frac{d[Mn(VII)]_{total}}{dt} = \{\frac{k'[LCO_2H]^{1/2} + k'_2[LCO_2H]_0}{[H^+]}\}$	103
9.	Aspartic acid	chloramine-T	alkaline medium	nitrile, ammonia & carbondioxide	$-\frac{d[CAT]}{dt} = \frac{2k_1k_2}{k_{-1}}.\frac{[CAT][S]}{[NaOH]}\{1+\frac{k_5k_4}{k_2k_4}[Hg(II)]\}$	107
10.	Serine, threonine, arginine, aspartic acid and glutamic acid	N-bromoace-tamide	alkaline medium	ammonia, alde-hyde carbon-dioxide	$-\frac{d[NBA]}{dt} = \frac{k_dK_1K_2[NBA][S][OH^-]}{1+K_1[OH^-]+K_1K_2[S][OH^-]}$	110
11.	Glycine, alanine, valine, leucine and phenyl-alanine	dichloramine-B	aquo-methanol	nitrile, amine & carbondioxide	$-\frac{d[DCB]}{dt} = \frac{K_1k_2[DCB]^2[S]}{[H^+]+K_1[S]}$	121

S.No.	Amino acids	Oxidant	Medium	Products	Rate Law	Ref.
12.	Glycine, alanine, ABA, NLE, NVA and phenyl-alanine	pyridinium hydrobromide perbromide	aqueous acetic acid	ammonia, carbondioxide & aldehyde	$-\frac{d[PHPB]}{dt} = \frac{k_2K[\text{amino acid}]^2[PHPB]}{1 + K[\text{amino acid}]^2}$	130
13.	Glycine, alanine, phenylalanine, valine, leucine and serine	diperiodato cuprate (III)	alkaline medium	aldehyde, ammonia & carbondioxide	$-\frac{d[DPC]}{dt} = k K_1K_2K_5[Cu(HL)_2][R\text{-}CH\text{-}COO^-]\cdot \frac{\{1+K_3([HL]+[OH^-])\}}{K_3K_4[OH^-][HL]\{1+K_1[OH^-]\}}$ (NH_2)	131
14.	Glycine, alanine, valine and leucine	potassium permanganate	aqueous sulfuric and perchloric acid media	ammonium ion carbondioxide & aldehyde	$-\frac{d[MnO_4]}{dt} = k[\text{amino acid}][MnO_4]$	132
15.	Glycine	Cerium (IV)	$HClO_4$ medium	ammonia, aldehyde, carbondioxide& amine	$\text{rate} = k_3K_3K_4[\text{Ceric}]\text{Glycine}][HClO_4][Ag^+]$	133
16.	Glutamic acid	chloramine-T	alkaline medium	nitrile	$-\frac{d[CAT]}{dt} = \frac{2k_1k_2[CAT][GuGA]}{k_{-1}[NaOH]}$	134
17.	Glycine, alanine & valine	chloramine-T	alkaline medium	nitrile, carbondioxide & amine	$-\frac{d[CAT]}{dt} = \frac{2k'_1k'_2[CAT][RCHNH_2COOH]}{k_{-1}[NaOH]}$	135

S.No.	Amino acids	Oxidant	Medium	Products	Rate Law	Ref.
18.	Glycine, alanine, valine and leucine	bromamine-T	acetate buffer	ammonia, carbon-dioxide & alde-hyde	$-\frac{d[BAT]}{dt} = \frac{k_3K_1[BAT]_0[S]}{1 + K_1[S]}$	136
19.	Alanine, valine and leucine	N-chlorobenz-amide	water-metha-nol mixture	aldehyde, ammonium ion & carbondioxide	$-\frac{d[NCB]}{dt} = \frac{k_1k_2[NCB][HCl][\text{amino acid}]}{k_{-1}[C_6H_5CONH_2]k_2[\text{amino acid}]}$	137
20.	Glycine, alanine, valine leucine and phenyl-alanine	bromamine-B	acetate buffer	ammonia, amine carbondioxide & aldehyde	$-\frac{d[BAB]}{dt} = \frac{k_2K_1[BAB]_0[S]}{1 + K_1[S]}$	138
21.	Glycine,alanine,leucine, isoleucine and phenyl-alanine	potassium bromate	acetic acid media	ammonium ion, aldehyde & carbondioxide	$-\frac{d[BrO_3]}{dt} = k[\text{bromate}][\text{amino acid}][H^+]^2$	139
22.	DL-methionic	bromamine-T	$HClO_4$, H_2SO_4 and NaOH	amine, carbon-dioxide	$-\frac{d[BAT]}{dt} = k[BAT][H^+]^2$ and $-\frac{d[BAT]}{dt} = \frac{k_1k_2[BAT][OH^-]}{k_{-1}[RNH_2] + k_2}$	140
23.	L-alanine, L-valine, L-leucine, L-serine, L-threonine, L-arginine, L-histidine, L-glutamic acid and L-glutamine	bromamine-T	alkaline medium	aldehyde,carbon-dioxide & ammonium ion	$-\frac{d[BAT]}{dt} = k[BAT] + k'[BAT][R'CH(NH_2)COO^-]$	141
24.	L-arginine	chloramine-T	$HClO_4$ medium	amine, carbon-dioxide,ammonia & aldehyde	$-\frac{d[CAT]}{dt} = k_4[CAT]H^+][Cl^-] + k_5[CAT][H^+][H_2O]$	142

S.No.	Amino acids	Oxidant	Medium	Products	Rate Law	Ref.
25.	Phenylglycine, phenylalanine, proline and hydroxyproline	peroxydisulfate	aqueous medium	ammonia, carbondioxide & aldehyde	$-\frac{d[S_2O_8]}{dt} = \left(\frac{k_1 k_3 k'_7}{k_9}\right)[S_2O_8][Ag^+]^{1/2} + \left(\frac{k_4}{2k_3}\right)[Cu^{2+}][Ag^+]$	143
26.	Alanine, glycine, phenylalanine, glutamic acid and aspartic acid	periodate	aqueous medium	aldehyde, ammonia & carbondioxide	$-\frac{d[P]_t}{dt} = \{k_1[H_4IO_6+IO_4] + k_2[H_3IO_6]\}[AA]$	144
27.	Glycine	Cerium (IV)	$HClO_4$ medium	formic acid, carbondioxide & ammonia	$-\frac{d[Ce(IV)]}{dt} = k_2K_3K_4[Ceric][Gly][HClO_4][Ag^+]$	145
28.	Glutamic acid	chloramine-T	HCl medium	amine, nitrile, & carbondioxide	$-\frac{d[CAT]}{dt} = \frac{2k_1k_2}{k_{-1}}[CAT][H^+][S^0]$	146
29.	Leucine, serine, glutamine and glutamic acid	chloramine-T	$HClO_4$ medium	amine, carbondioxide & nitrile	$-\frac{d[CAT]}{dt} = \frac{k_1k_2[SH^+][RNHCl]}{k_{-1}[H^+]}$	147
30.	Serine, methionine and cysteine	chromic acid	$HClO_4$ medium	aldehyde, carbondioxide & ammonia	$-\frac{d[CrO_3]}{dt} = k$ [chromic acid][substrate][H^+]	148
31.	Glycine, phenylalanine, leucine, valine and alanine	phenyliodosyl acetate and lead tetracetate	acetic and $HClO_4$ medium	carbondioxide, ammonia & aldehyde	$-\frac{d[PIA]}{dt} = \frac{k[S]_T[PIA]}{1 + K[H^+]}$	149
32.	α-aminobutaric acid, isovaline & leucine	manganese (III) sulfate	H_2SO_4 media	ammonia, aldehyde & carbondioxide	$Rate = \frac{k_1k_2k_3[A][Mn^{3+}]^2}{k_{-1}k_{-2}[H^+][Mn^{2+}] + k_{-1}k_3[Mn^{3+}][H^+]}$	150

S.No	Amino acids	Oxidant	Medium	Products	Rate Law	Ref.
33.	L-arginine	potassium permanganate	sulfuric acid medium	ammonium ion, carbondioxide & aldehyde	$-\frac{d[MnO_4]}{dt} = k\,[\text{amino acid}]\,[MnO_4]$	151
34.	Alanine, valine, leucine, glutamic acid and aspartic acid	hexacynanoferrate (III)	alkaline media	aldehyde, ammonia & carbondioxide	$-\frac{d[Fe(CN)_6]}{dt} = \frac{2\,k_2\beta_2\,[OH^-][Os(VIII)]_0\,[RCH(NH_2)CO_2]}{1+\beta_2\,[RCH(NH_2)CO_2]}$	64
35.	Glycine, phenylalanine and alanine	lead tetracetate	acetic acid	aldehyde, carbondioxide & ammonia	$-\frac{d\ln[LTA]}{dt} = \frac{k\,K\,[AA]\,[LTA]}{1+K\,[AA]}$	153
36.	Methionine	chloramine-T	HCl, $HClO_4$, H_2SO_4 and NaOH	toluene-p-sulphonamide methionine sulphone & carbondioxide	$-\frac{d[CAT]}{dt} = k\,[CAT]\,[H^+]$ and $-\frac{d[CAT]}{dt} = \frac{k_{10}\,k_{11}[CAT]\,[Mt]}{k_{-10}\,[OH^-]} + k_{13}[CAT][Mt]$	154
37.	Leucine, glutamine, arginine, histidine and threonine	chloramine-T	$HClO_4$ medium	amine, carbondioxide & nitrile	$-\frac{d[CAT]}{dt} = \frac{k_x\,[\text{Threonine}]\,[CAT]^2}{[H^+][RNH_2] + k_y\,[Cl^-][CAT]}$	155

CHLORAMINE-T

CHLORAMINE-T USED AS OXIDIZING AGENT

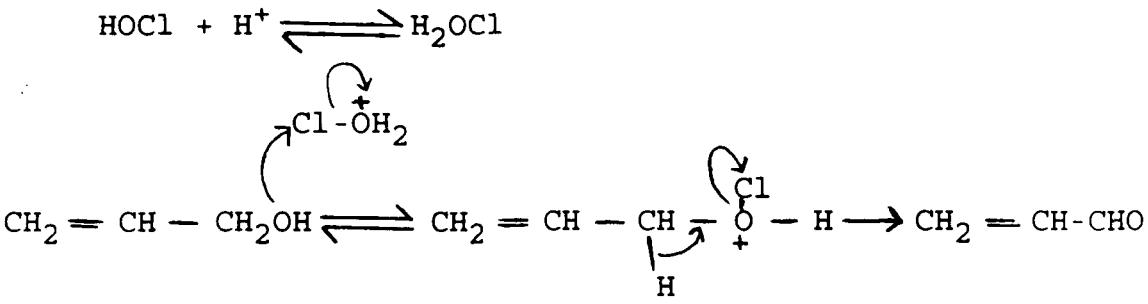
Since its synthesis, chloramine-T and related aryl sulfonamide derivatives have got potential applications in the varying field ranging from disinfectant, antiseptic and its reactivity with other functional groups. Chloramine-T and its related compounds are extensively used as analytical reagents. The diverse mode of action of N-halogeno-N-metallo reagents (chloramine-T and related aryl sulfonamide derivatives) is attributed to their ability to act as sources of (a) halonium cations (x^+) (b) hypohalite species (HOX) (c) anions (e.g., sulfonamidate or carbamidate anions) which act both as bases and nucleophiles, and (d) nitrenoids has been significant. These reagents are stable in aqueous solution and behave as strong electrolytes acting as strong oxidants in both acidic and alkaline media. As a result extensive studies related to the oxidation of a variety of functional groups are reported in the literature. The studies include the oxidation of sulfur compounds[160-163] (Sulfides, Selenides, Sulfoxides, and Sulfimides), nitrogen compounds[164-167] (Nitroso, Nitro, Azo groups, Diaryldiazomethanes, Diarylhydrazones, α-amino acids and Isonitriles).

Chloramine-T reacts with the functional groups containing oxygen (e.g. alcohols, aldehydes, ketones, Phenolexpoxides etc.). Extensive studies of the kinetics and mechanism of chloramine-T oxidation of alcohols to aldehydes in alkaline, neutral, and acidic conditions have appeared[168-174]. Certain alcohol oxidations were catalyzed by Osmium (VII)[170]. In acid media, primary alcohols are oxidized to the aldehydes by chloramine-T via initial protonation to give N-chlorotoluene-p-sulfonamide, followed by a rate-determining hydrolysis to give hypochlorous acid. The reaction followed zero order dependence on alcohol and first order dependence on acid. The oxidation of allylic alcohol[171,173] suggested that protonated hypochlorous acid was the active oxidant and that 1,2 -elimination of HCl from the alcohol hypochlorite occurred. The first order dependence on allylic alcohols becomes independent of alcohol concentration in stronger acidic media. The oxidation of secondary alcohol[175] in strong acidic media gives the following rate equation.

$$- d\,[CAT]/dt = k\,[CAT]\,[alcohol]\,[H^+]^2$$

The rate law, low kinetic isotope effect, and effect of solvent polarity on the rate agreed with a mechanism involving rate determining reaction of either protonated chloramine-T (N-chlorotoluene-p-sulfonamide) or protonated

hypochlorous acid with the alcohol, giving the alcohol hypochlorite, followed by fast decomposition to ketone.



The observed order of 1.5 in hydrochloric acid was interpreted by simultaneous oxidation by Cl^+ or hypochlorous acid and protonated chloramine-T. In a low-percentage acetic acid medium the oxidation was second order in chloramine-T and first order in alcohol, under these conditions N, N-dichlorotoluene-p-sulfonamide is suggested as the active oxidant.

The oxidation of aldehydes by alkaline chloramine-T whereas in alkaline medium both enolizable and non-enolizable aldehyde is effected by the presence and absence of Osmium (VIII). Oxidation by chloramine-T is catalyzed by the presence of Osmium (VIII) but in acidic medium[176-178]. Aldehydes which are capable of enolization can be oxidized. It was suggested[179] that an "activated complex" facilitated the ability of chloramine-T to abstract a hydride ion from the hydrated aldehyde.

Alkaline chloramine-T oxidizes, carbohydrates[180]. e.g. xylose, arabinose, mannose and ribose to the corresponding aldonic acids. The oxidation of D(+)-sorbose[181] showed a brief induction period in a highly alkaline medium. The order with respect to hydroxide was found to be fractional.

Phenols react with chloramine-T to yield chlorination product[181-185]. A detail study[184] of cresol chlorination by chloramine-T between pH 6.82 and 2.10 showed second order kinetics, with rate constants in the order p-chlorophenol < P-cresol <o-cresol < phenol < m-cresol.

Recently, it has been reported[186] that chloramine-T is a potentially more exhaustive oxidizing agent in degradation of rubber than Cl. It results into more extensive damage to rubber gas kets and other rubber parts if in chloramine-T is treated water supply systems. The effect of chloramine was studied by measuring negative changes in tensile strength, swelling, surface cracking, and aging resistance of several rubber compounds containing EPDM, natural neoprine, nitrile, butadiene, fluoro and silicone rubbers.

The biological application of chloramine-T has been found[187] in the radiolabelling of bioactive molecules by halogenation. CAT may be used either as a solution or in

an immobilized from (Iodobeads) to release radioactive elemental iodine or other halogens by oxidation of their salts. CAT has a very high chlorine potential, and it causes oxidative degradation of peptide linkage in proteins. In some cases, the substrates are completely destroyed. To reduce the chlorine action of CAT, morpholine is mixed with CAT prior to exposure to the substrates. The N-chloromorpholine thus formed reacts with KI to give I_2. The reaction is found to be rapid. The low reactivity of moropholine with CAT is exhibited by oxidation degradation of 1 - amino cyclohexane carboxylic acid (a model amino acid) which decomposed rapidly in the presence of CAT, but there was no decomposition in the presence of N-chloromorpholine. N-chloromorpholine was compared to CAT solution and Iodobeads for the iodination of L-tyrosine. When the effect of CAT alone was compared with mixture of CAT and morpholine for the iodination of a model peptide, leucine enkephalin, it was found that the mixed CAT produced larger amounts of iodoleucine enkephalin and diiodoleucine enkephalin. It is proposed that the method employing N-chloromorpholine (which is produced insitu instantaneously) to release diatomic iodine is more convenient and efficient for radiolebelling peptides and proteins than methods currently used.

The reaction of choloramine-T with amino acid and related compounds[188] (B-alanine, L-alanine, and L-alanine ethyl ester) under pseudo first order conditions (where amino acids in large excess over CAT) showed that the over all reaction was second order. The rate of reaction was found to be independent of pH in the range of 6.1 to 8.5, and decreased with increasing pH above 8.5. The pH dependency was rationalized by assuming that unionized CAT reacts with the unionized amino groups of amino acid. A cyclic transition state involving a water molecule is proposed as reaction intermediate.

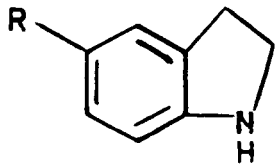
The oxidation of oxalic acid[189] by trichloro-melamine (TCM) and chloramine-T (CAT) follows second order kinetic in [TCM] while the rate is independent of [S] and $[H^+]$ concentrations. In CAT oxidation, the dependence on CAT and oxalic acid is unity each, whereas, the dependence on $[H^+]$ is zero. Solvent effect is different in the two cases, in the former case acceleration is observed with increase in percentage of acetic acid reaching a limiting value at higher percentage of acetic acid.

The ruthenium (III) catalyzed[190] oxidation of maleic and acrylic acid by chloramine-T in alkaline medium showed first order dependence of rate with respect to oxidant and the catalyst concentrations.

Jinxin[191] et al. reported the flow injection kinetic spectrophotometric method for the determination of trace iodine in geological samples using CAT. Iodide is oxidized with chloramine-T producing iodine which catalyzes oxidation of tetrabase to quinone and followed by rapid coupling reaction of quinone and tetrabase to develop a blue colour reaction product, which can be measured at 605 nm. The detection limit of the method is $0.08X10^{-6}$.

The oxidation of p-cresol[192] by chloramine-T in the presence of cetyltrimethylammonium bromide (CTAB) showed first order dependence on the oxidant concentration, but it has zero order with respect to p-cresol. Ionic strength and presence of halide ion have no effect on the rate, but the reaction is catalyzed by mercuric ion.

The kinetics of oxidation of indoles[193] to corresponding oxindole by N-chloro-N-sodio-p-toluene sulfonamide in alkaline medium is catalyzed by osmium (VIII) at 30° showing first order dependence each in chloramine-T, Os (VIII) and indole (I) (R = H).



(I)

An isokenetic relationship was observed with β = 325, indicating enthalpy as the rate controlling factor.

The kinetics of oxidation of EDTA[194] by chloramine-T in the presence and absence of a cationic surfactant, CTAB shows that the reaction is first order in CAT and fractional order in [EDTA]. Addition of reaction has an appreciable effect on the reaction rate. Addition of sodium sulfate and Hg^{++} ion cause enhancement of reaction rate.

The kinetics of reaction of benzoic acid, 2-chlorobenzoic acid, 2-bromobenzoic acid, and 2-nitrobenzoic acid by bromamine-T (BAT) in aqueous acetic acid-perchloric acid media in the presence of Ru (III) chloride was studied by Pati and Sahu[195]. The reaction follows first order kinetics each in [BAT] and [Ru(III)], fractional order in [perchloric acid], and is independent of substrate concentration. The authors also reported the effect of variation of ionic strength and dielectric constant of the medium on the rate and have proposed a suitable mechanisms.

Oxidation of acetyl acetone[196] (AA) by chloramine-T (CAT) and bromamine-T (BAT) in the presence of HCl at constant ionic strength at 303-318 K obeys the rate law, rate = $k\,[OX]\,[AA]^x\,[HCl]^y$ where $x < 1$ and $y < 1$. The rate increases in D_2O medium. The authors have observed Michaelies-Menten type of kinetics and computed the

activation parameters of the reaction step. The authors also proposed that the mechanism involves simultaneous catalysis by H^+ and Cl^- ion and interaction of haloamine species with the enol gives the diketone.

Kinetics of chlorination of several benzaldehyde anils ($PhCH{:}NC_6H_4X$, where X = H, m-Cl, p-Cl, m-COOH, p-COOH, m-NO_2, p-NO_2, p-CH_3 and 3,4-dichloro) by chloramine-T (CAT) in aqueous methanol (1:1 v/v) medium has been investigated by Hegde and Gowda[197]. The rate versus $[H^+]$ plots show L-shaped profiles with the substrates such as the anil parent and these substituted at m-Cl, p-Cl, m=COOH and p-CH_3, while the other anils except p-NO_2 show inverted L-shaped profiles. The reaction generally shows first order depen[illegible]ce in [CAT], and fractional order to first order in [anil]. At low hydrogen ion concentration the reaction is first order in [CAT] and fractional order each in [anil] and $[H^+]$ with p-COOH, m-NO_2 and 3,4-dichloro substituted anils. Anilines produced by the hydrolysis of anils react with the oxidant to give respectively chloro derivatives at ortho or para position.

The kinetics of chlorine transfer from chloramine-T (CAT) to several amines are second order and independent of p-toluenesulfonamide concentration thus, the reaction dos not involve disproportionation of CAT to dichloramine-

T. The mechanism of the reaction involves (1) ionized species of CAT with the ionized amine (ionic mechanism) or (2) unionized species of CAT with the unionized amine (nonionic mechanism). The second order, pH independent rate constants for the ionic and nonionic mechanism were reported[198] to be 1.6 and $5X10^6$ M^{-1} S^{-1}, respectively. Lewis and Hussain suggested that nonionic mechanism is similar to chlorination reactions involving nonionizable chloramines, such as N-chlorosuccinimide, N-chloroquinuclidine, and N-chloro-N-methyl-benzenesulfonamide. It appears that the mechanism for Cl exchange involves a molecule of water in a cyclic, six-membered transition state.

Kinetic of oxidation of D-cycloserine[199] by chloramine-T in HCl medium follows first order kinetic each with respect to [CAT] and [HCl], and fractional order in the concentration of the substrate. Hydrogen and chloride ions catalyzed the reaction simultaneously.

Kinetics of oxidation of oxalic acid with chloramine-T was studied by Sharma[200] et al. in acid perchlorate medium is second order. The reactive chloramine-T species in monochloramine-T that reacts with molecular and ionized forms of oxalic acid. The effect of hydrogen ion concentration on the reaction rate correlates with oxalic acid and not with the chloramine-T species. A comparative

treatment of activation parameters suggests C-C scission of the acid.

The reaction of 1-and 2-naphthylamines[201] with chloramine-T in aqueous acetic acid-perchloric acid medium is reported to follow a pseudo-first order of reaction is fractional in [substrate] and it becomes first order at higher concentrations. The order with respect to [$HClO_4$] varies, approaching a limiting value at 1.0 M $HClO_4$. The stoichiometry of the reaction, i.e. [substrate]/[CAT] is 1:2 and 1:4.

Mehrotra[202] observed the reaction between 2-propanol and chloramine-T follows first order dependence in [CAT] and [H^+]. The rate was found to be independent of 2-propanol concentrations.

Lalitha and Sethuram[203] studied the oxidation of 1- and 2- propanol by chloramine-T in the presence of ruthanium (VI) as catalyst and observed that the reaction is first order in [Ru (VI)] and zero order in [CAT]. The reaction rate increases with increasing [substrate] and exhibits Michaelies-Menten behavior. The rate data suggest that oxidation proceeds via a 1:1 Ru (VI)-2-propanol complex which slowly disproportionates into acetone and Ru (IV).

Gowda[204] et al. observed that the oxidation of carbohydrazide by chloramine-T in aqueous $HClO_4$ medium follow first order kinetic in [CAT] and fractional in the concentration of the substrate. The dependence in $[H^+]$ is complex the rate was zero to fractional order in $[HClO_4]$ range used. The proposed mechanism is

$$ArSO_2NHX + H_2NHNCONHNH_2 \overset{K_1}{\rightleftharpoons} (Ar\ SO_2\ NHXNHNHCONHNH_2) + H^+ \quad \text{(fast)}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (Y)$$

$$Y \xrightarrow{k_2} ArSO_2\ NH^- + \underset{(S)}{H_2NHNCONHNHX} \quad \text{(slow)}$$

$$ArSO_2\ NHX \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ar\ SO_2\ NH^- + X^+ \quad (k_3 \text{ is slow})$$

$$X^+ + S \longrightarrow S' + H^+ \quad \text{(fast)}$$

$$Ar\ SO_2\ NH^- + H^+ \longrightarrow Ar\ SO_2\ NH_2 \quad \text{(fast)}$$

$$ArSO_4NHX + S \xrightarrow{k_4} S' + ArSO_2NH_2 \quad \text{(slow)}$$

$$S' + Ar\ SO_2\ NHX \longrightarrow XHNHNCONHNHX + Ar\ SO_2\ NH_2 \quad \text{(fast)}$$

$$XHNHNCONHNHX + 2Ar\ SO_2\ NHX \longrightarrow \text{final products}$$

where Ar = p - $CH_3\ C_6\ H_4$

The kinetics of oxidation of p-, m- and o-HOC_6H_4CHO with chloramine-T in 20% MeOH catalyzed by Ru (III) was studied by Ali and Upadhyay[205]. The order of reaction in chloramine-T was unity, that in substrate and acid concentration is fractional. The reaction rate is

proportional to ($k' + k''$ [$RuCl_3$]), where k' and k'' are constants associated with catalyzed and uncatalyzed steps.

Kinetics of oxidation of H_2 NN:C(SH) $NHNH_2$ (TCH), $Zn(THC)_2Cl_2$ and MeCH : NNHC(S) CHNN : HCMe[206] by chloramine-T in 1:1 (v/v) H_2O-MeOH and H_2O-HOAC media in the presence of $HClO_4$ showed first order dependence in [oxidant] and varying fractional order in [substrate]. Oxidation of TCH and its complex in H_2O-MeOH media showed fractional order kinetics in [H^+], while oxidations of the hydrazone in H_2O-MeOH media and TCH in H_2O-ACOH medium showed inverse fractional order kinetics in [H^+]. Variation in solvent components had considerable effect on oxidation rates, but the effect was more pronounced in H_2O-ACOH medium. Addition of the reduced product of the oxidant had no significant effect on the rates of reactions.

Mythily[207] et al. studied the oxidation of cinnamaldehyde (cinn) by chloramine-T (CAT) in HCl and H_2SO_4 medium and has proposed the following rate law

$$(1) \quad - \frac{d[CAT]}{dt} = k[CAT]\,[cinn]^x\,[H^+]\,[Cl^-] \text{ and}$$

$$(2) \quad - \frac{d[CAT]}{dt} = k''\,[CAT]\,[cinn]^y[H^+]^z$$

The value of x=varies from 0.9 to zero, while the values of y and z are 0.83 and 0.72 respectively. The authors have also studied the effects of ionic strength, reaction product (p-toluenesulfonamide), dielectric constant of the solvent medium, at different [Cl^-] and [SO_4^-] on the reaction rate.

The Osmium (VIII) catalyzed oxidation of cinnamaldehyde[208] by chloramine-T in alkaline medium follows first order kinetics each in [CAT] and [Os (VIII)] and inverse first order in [OH^-]. In acid medium, however, Michaelies-Menten kinetics is obeyed under pseudo first kinetic condition with respect to [CAT] and a fractional order in [aldehyde] which becomes zero at higher [aldehyde].

Kinetics of oxidation of hydrazides by chloramine-T (CAT) has been investigated by Nimbalkur[209] in 50% (v/v) aqueous methanol medium. The rate followed first order kinetics in [CAT] and [hydrazide].

The kinetic study of Hg (II)- catalyzed oxidation of asparagine by chloramine-T in aqueous NaOH by Sengar and Yadav[210] shows a first order dependence on chloramine-T and asparagine concentrations and an inverse first order dependence on alkali concentration. At high alkali concentrations, the reaction is not dependent on alkali

concentration. The rate of disappearance of chloramine-T follows a first order dependence in [Hg (II)].

The kinetics of chlorination of p-aminobenzoic acid[211] by chloramine-T in the presence of hydrochloric acid is catalyzed by [H^+] and [Cl^-]. The reaction follows the first order kinetics in [CAT] but half-order each in [H^+], [Cl^-] and substrate concentration. Variation in the ionic strength and dielectric constant and addition of the reaction product, p-toluenesulfonamide, had negligible effect on the rate reaction. The authors proposed a mechanisms in which reversible complex between the acid form of chloramine-T and the substrate was formed. The complex, in a rate determining step, is attacked by H^+ and Cl^- to form another intermediate which will undergo electronrearrangement to form the final products.

The kinetics of oxidation of aliphatic amines ($EtNH_2$, $BuNH_2$, iso-$prNH_2$, Et_2NH and Et_3N) by chloramine-T were studied by Gupta[212] et al. in NaOH medium catalyzed by Osmium (VIII) and in $HClO_4$ medium ruthenium (III) was used as catalyst. The authors reported the order of reaction in [chloramine-T] is unity and zero order in [OH^-]. For the Osmium (VIII) catalyzed oxidation [OH^-] and [primary amine] produced a retarding effect. The ruthenium (III) catalyzed oxidation of primary amines followed similar kinetics. The order of reactions in [amine] and [acid]

decreased from unity at higher amine or acid concentration.

Ramakrishna and Kandlikar[213] observed the catalytic effect [iridium (III) + vanadium (IV)] is greater than that of Ir (III) or V (IV) used alone in the oxidation of mono-, di- and trichloro-acetic acids by chloramine-T. The oxidation of substituted acetic acid involves formation of an $[Ir\text{-substrate}]^{3+}$ complex, which later reacts with HOCl in the rate determining step.

The studies on the kinetics of oxidation of thiosemicarbazide (TSC) and its hydrazone (benzaldehyde thiosemicarbazone) by chloramine-T (CAT) and dichloramine-T (DCT) in aqueous methanol containing perchloric acid was carried out by Gowda and Sherigara[214]. Oxidation of TSC by both the oxidants showed first order dependence in [oxidant] fractional order in [TSC] and nearly inverse first order in $[H^+]$. The dependence in [TSC] changes from fractional order to zero order in both CAT and DCT oxidations. The rate followed inverse fractional order kinetics in $[H^+]$ in both the bases. Oxidation of TSC with both the oxidants follows a Michaelies-Menten mechanisms.

The kinetic of oxidation allyl, crotyl and cinnamic alcohols by chloramine-T (CAT) was studied by Naidu[215]

et al. The following rate law has been given $r = k\,[CAT]\,[H^+]^{-1}$. The reaction appears to follow a mixed-order kinetics with simultaneous catalysis by $[H^+]$ and SO^{2}_{4} ions. The proposed mechanism is

$$(TsNH_2\ Cl)^+ \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} Ts\ NHCl + H^+$$

$$TsNHCl + H_2O \xrightarrow[\text{slow}]{k_2} TsNH_2 + HOCl$$

$$HOCl + \text{alcohol} \xrightarrow[\text{fast}]{k_3} \text{Products}$$

Scheme - 1

The catalytic influence of sulfate ion can be rationalized by scheme 2

$$(TsNHCl)^+ \overset{K_1}{\rightleftharpoons} TsNHCl + H^+$$

$$(TsNHCl) + SO^{2-}_{4} \underset{\text{fast}}{\overset{K_4}{\rightleftharpoons}} TsNHCl \text{ ----- } SO^{2-}_{4}$$

(X)

$$X + H_2O \xrightarrow[\text{slow}]{k_5} HOCl + TsNH_2 + SO^{2-}_{4}$$

$$HOCl + \text{alcohol} \xrightarrow[\text{fast}]{k_6} \text{Products}$$

Scheme - 2

The oxidation of ornithine monohydrochloride[216] with chloramine-T catalyzed by Cu (II) and Hg (II) in alkaline

medium shows a first order dependence on both [chloramine-T] and ornithine monohydrochloride and inverse first order dependence on alkali. The reaction is also first-order dependence on both [Cu (II)] and [Hg (II)]. In the presence of Cu (II), the oxidation takes place both by uncatalyzed and catalyzed paths, but in the presence of Hg (II), the uncatalyzed oxidation path is completely oblished.

The kinetic of copper (II) catalyzed oxidation of asparagine[217] by chloramine-T in aqueous NaOH follows first order in [chloramine-T] and in [asp] and inverse first order in [OH^-]. The reaction proceeds through both catalyzed and uncatalyzed pathways. The proposed by Sengar et al.

$$Cu^{II} + Asn^- \overset{K_{eq}}{\rightleftharpoons} Cu - Asn \text{ (complex)}$$

$$CAT + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CAT' + NaOH$$

$$Asn^- + CAT' \xrightarrow{k_2} X$$

$$Cu - Asn + CAT' \xrightarrow{k_3} X + Cu^{II}$$

$$X + CAT' \xrightarrow[fast]{k_4} Products$$

The rate expression is

$$-\frac{d\,[CAT]}{dt} = 2k_1/k\text{-}1\ [CAT]/[NaOH]\ \{k_2\ [Asn^-] + k_3\ [Cu - Asn]\}$$

OXIDANT : CHLORAMINE-T

S.N.	Substrates	Rate Law	Active species	Ref.
1.	D (-) ribose	$-\frac{d[CAT]}{dt} = \frac{k_3 k_5 [S][CAT][OH^-]^2}{k_{-3}[H_2O] + k_5[CAT][OH^-]}$	$CH_3C_6H_4SO_2NHCl$, ClO^-	174
2.	n-butanol isobutanol & isopentanol	$-\frac{d[CAT]}{dt} = \frac{k_2 k_3 [H_2O]}{k_{-2} + k_3[H_2O]}[CAT][H^+]$	$CH_3C_6H_4SO_2NHCl$, $CH_3C_6H_4SO_2NH_2$ and HOCl	179
3.	Formaldehyde and acetaldehyde	$-\frac{d[CAT]}{dt} = \frac{k_2 k_3 [CAT][Os(VIII)][H_2O]}{k_{-2} \quad NaOH}$	$CH_3C_6H_4SO_2NHCl$,	176
4.	Xylose, arabinose, mannose & galactose	$-\frac{d[CAT]}{dt} = \frac{k_2 k_3 [S][ClO^-][OH^-]^2}{k_{-2}[H_2O] + k_3[ClO^-][OH^-]}$	OCl^-, HOCl and $[OH^-]$	180
5.	D (+) Sorbose	$-\frac{d[ClO^-]}{dt} = \frac{k_3 k_5 [S][ClO^-][OH^-]^2}{k_{-3}[H_2O] + k_5[ClO^-][OH^-]}$	ClO^-	181
6.	Cresol	$1/\frac{d[CAT]}{dt} = \frac{1}{k_q[CAT]^2}\left(\frac{k_{-d}[TSA]}{k_2[p\text{-cresol}]} + 1\right)$	HOCl and $CH_3C_6H_4SO_2NH_2$	182

S.N.	Substrates	Rate Law	Active species	Ref.
7.	Acetylaceton	$-\frac{d[OX]}{dt} = \frac{k_3 k_1 k_2[OX]+[AA]_0[H^+][Cl^-]}{1+K_1[H^+][Cl^-]+K_1 K_2[AA]_0[H^+][Cl^-]}$	RNXH, RNX_2 and HOX	196
8.	Thiocarbohydrazide	$-\frac{d[CAT]}{dt} = \frac{K_1 K_2 k_3 [CAT]_t [S][H^+]}{1 + K_1[H^+] + K_1K_2[S][H^+]}$	$ArSO_2NCl^-$, $ArSO_2NHCl$, HOCl and $ArSO_2NCl_2$ at low $[H^+]$ $ArSO_2NH_2Cl$ and H_2OCl at High $[H^+]$	206
9.	Carbohydrazide	$-\frac{d[oxidant]}{dt} = \frac{K_1k_2[oxidant][S]}{[H^+]} + k_3[oxidant]$	$ArSO_2NHX$, $ArSO_2NX_2$ and HOX at low $[H^+]$ $ArSO_2NH_2X^+$ and H_2OX^+ at High $[H^+]$	204
10.	Cinnamaldehyde	$-\frac{d[CAT]}{dt} = \frac{k_6K_1K_4K_5[CAT]_t[S][Cl^-]}{1+K_1+K_1K_4[Cl^-] + K_1K_4K_5[Cl^-][S]}$	$ArSO_2NHCl$ (acid medium)	208
		$-\frac{d[CAT]}{dt} = \frac{k_8K_7[Os(VIII)][CAT][H_2O]}{[OH^-]}$	$ArSO_2NHCl$ and $HOCl^-$ (alkaline medium)	213
11.	Mono-, Di and Trichloroacetic acid	$-\frac{d[CAT]}{dt} = Kk_3[CAT][V(IV)][H^+]$	RNHCl, RNH_2Cl	___

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EXPERIMENTAL

MATERIALS :

The following reagents and their respective grades were used during the kinetic and mechanistic studies of oxidation of glycine and DL-alanine by Sodium-N-chloro-p-toluenesulfonamide (chloramine-T) in the absence and presence of detergents. No further purification of reagents was done.

TABLE-1 : LIST OF REAGENTS

Name	Symbol used	Grade	Supplier
Glycine	Gly	LR	Ranbaxy Laboratories, India
DL-Alanine	Ala	LR	Sisco Research Laboratories, India
Chloramine-T	CAT	GR	Loba chemie, India
Sodium dodecyl sulfate	SDS	AR	BDH-England
Cetyl pyridinium chloride	CPC	GR	Loba Chemie, India
Hydrochloric acid	HCl	LR	E. Merck, India
sodium perchlorate	$NaClO_4$	GR	Loba chemie, India
Sodium thiosulfate	$Na_2S_2O_3$	GR	Loba chemie, India
Starch		GR	Loba chemie, India
Potassium iodide	KI	GPR	E. Merch, India
Sodium iodide	NaI	GR	Loba chemie, India

PURIFICATION OF SODIUM DODECYL SULFATE AND CETYL PYRIDINIUM CHLORIDE :

Sodium dodecyl sulfate (SDS) and cetyl pyridinium chloride (CPC) were used without further purification because limited runs of kinetics experiments with purified SDS (Duynstee and Grunwd)[1] and purified CPC (by recrystallized twice from an ethanol-ethyl acetate mixture and dried at 60°C under moderate vacuum) showed no significant difference.

PREPARATION OF STOCK SOLUTIONS

For the preparation of the stock solutions doubly distilled water was used as solvent. Chloramine-T (CAT) was measured iodometrically against standardized thiosulfate. The calculated amount of solid SDS was added directly to the substrate solution. Stock solution of 0.05 mol dm^{-3} CPC was prepared and its required volume was used in a particular run. Ionic strength was maintained by addition of sodium perchlorate ($NaClO_4$). Kinetic experiment were performed under the varying conditions of [substrate], $[H^+]$, $[NaClO_4]$, [SDS], [CPC] and temperature. The concentration of oxidant was kept constant at 0.002 mol dm^{-3} through out the kinetic experiments, as the variation in [oxidant] itself had no effect on the observed rate constant. All the kinetic runs were carried out under pseudo-first order reaction condition.

ANALYSIS OF PRODUCTS :

For identification of the products, the calculated amount of chloramine-T (CAT) and acidified solution of amino acid were mixed together under the reaction conditions identical to the kinetic experiment. The reaction mixture was kept over night at 30°C. The presence of aldehyde in the product was detected by their characteristic colour reaction with Schiff's reagent[2]. The evolution of ammonia was confirmed by the reaction with the Nesseler's reagent[3]. The presence of amine was detected by carbylamine test.

Carbondioxide evolved during the oxidation of amino acids in the absence and presence of surfactants was measured volumetrically on passing through the pyrogallol solution interceptors, there was no change in the amount of gas evolved under different conditions for the oxidation of glycine. However, in the case of alanine, the amount of gas evolved decreased on passing through the pyrogallol solution indicating presence of oxygen as end product. Thus the presence of aldehyde, ammonia, amine and CO_2 as product is in conformation with the studies of the other workers[4-9].

STOICHIOMETRY

Varying ratios of amino acids to CAT was mixed in HCl medium at 30°C and kept for 24 hours. Estimation of unreacted CAT (as determined iodometrically) showed that one mole of each amino acid, glycine and alanine, consumed one mole of CAT as reported by Gowda and Lakshimi Rao[10].

$$R'CH(NH_2)COOH + RNCl\,Na + H_2O \longrightarrow R'CHO + CO_2 + RNH_2 + NH_3 + Na + Cl^-$$

Where, $R = CH_3C_6H_4SO_2$

and

$R' = H$ (Gly) and CH_3 (Ala)

KINETIC RUNS

All the reactions were carried out in glass stoppered corning conical flask at the required temperature. The temperature was maintained in a thermostated water bath at ± 0.1°C of desired value.

Kinetic experiments were performed under pseudo-first order conditions employing 10-fold (or greater) excess of amino acid over CAT. Duplicate kinetic runs showed that the rates were reproducible to within ± 5 %. The pseudo-first order rate constnat, k_{obs} (s^{-1}) was computed from the linear ($r > 0.980$) least squares plot of log R versus time (where R is the micro burette reading). Requisite

amount of amino acid, hydrochloric acid and sodium perchlorate were taken in a conical flask and measured amount of CAT solution was taken in another flask. The two flask were thermally equilibrated for 15 minutes in the thermostated water bath. Then CAT solution was added to the flask containing amino acid solution and was mixed thoroughly by shaking. The progress of the reaction was followed by measuring the unreacted CAT (by iodometrically method) in a measured aliquot (10 ml) of the reaction mixture at various time intervals. The reaction was studied upto 80% consumption of CAT.

To study the effect of SDS, kinetic experiments were performed as discussed earlier except that required amount of SDS was added as solid directly to the flask containing amino acid solution. The effect of CPC was studied by using appropriate amount of CPC solution. To maintain ionic strength in the presence of SDS and CPC micelles, $NaClO_4$ was used.

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MEASUREMENT AND RATE CONSTANTS

OXIDATION OF GLYCINE IN THE ABSENCE OF SURFACTANTS

Tables 2 to 7 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$).

The concentration of glycine was varied from 0.03 to 0.12 $moldm^{-3}$, at a fixed [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[H^+]$ = 0.05 $moldm^{-3}$, u = 0.20 $moldm^{-3}$ and at different temperature (30° to 40°C).

Tables 8 to 17 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$).

The concentration of hydrogen ion is varied from 0.04 to 0.20 $moldm^{-3}$, at a fixed [CAT] = 2 x 10^{-3} $moldm^{-3}$, [Gly] = 0.03 $moldm^{-3}$, u = 0.20 $moldm^{-3}$ and at different temperature (30° to 40°C).

Table - 2 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.86	0.686	4.70	0.672	4.48	0.651
10	4.52	0.655	4.30	0.633	3.80	0.579
15	4.20	0.623	4.00	0.602	3.22	0.508
20	3.82	0.582	-	-	2.74	0.438
25	-	-	-	-	2.32	0.365
30	3.28	0.516	3.02	0.480	1.94	0.288
35	-	-	-	-	1.68	0.225
40	2.84	0.453	-	-	1.46	0.164
45	-	-	2.46	0.391	1.26	0.100
50	2.38	0.376	-	-	1.16	0.064
60	2.00	0.301	1.84	0.265	-	-
75	1.56	0.193	1.38	0.139	-	-
80	-	-	1.24	0.093	-	-
85	-	-	1.16	0.064	-	-
90	1.30	0.114	1.00	0.000	-	-
	$^{01}k_{obs}=2.68\times10^{-4}s^{-1}$		$^{01}k_{obs}=3.07\times10^{-4}s^{-1}$		$^{01}k_{obs}=5.18\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table - 3 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
2	-	-	4.80	0.681	4.86	0.687
5	4.34	0.637	4.14	0.617	4.16	0.619
7	-	-	3.64	0.561	3.58	0.553
10	3.52	0.546	3.14	0.497	3.04	0.483
12	-	-	-	-	2.64	0.422
15	2.84	0.453	2.36	0.373	2.24	0.350
17	-	-	-	-	2.00	0.301
20	2.32	0.365	1.86	0.269	1.68	0.225
25	1.90	0.279	1.48	0.170	1.30	0.114
30	1.56	0.193	1.18	0.072	1.20	0.079
35	1.26	0.100	-	-	-	-
40	1.10	0.041	-	-	-	-
	$^{01}k_{obs}=6.52\times10^{-4}s^{-1}$		$^{01}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{01}k_{obs}=9.59\times10^{-4}s^{-1}$	

Temp = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}

$[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [surfactants]=Nil.

Table - 4 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	4.90	0.690	-	-	4.74	0.676
5	4.76	0.677	4.66	0.662	4.42	0.645
8	-	-	-	-	3.80	0.579
10	4.24	0.627	4.00	0.602	3.46	0.539
13	-	-	-	-	2.96	0.471
15	3.70	0.568	3.50	0.544	2.70	0.431
20	3.30	0.518	3.08	0.488	2.06	0.313
25	2.86	0.456	2.62	0.418	1.68	0.225
30	2.54	0.405	2.24	0.350	1.34	0.127
35	-	-	1.82	0.260	1.12	0.049
40	1.92	0.283	1.54	0.187	-	-
45	-	-	1.30	0.114	-	-
50	1.44	0.158	1.16	0.064	-	-
60	1.12	0.049	-	-	-	-
	$^{01}k_{obs}=4.22\times10^{-4}s^{-1}$		$^{01}k_{obs}=4.99\times10^{-4}s^{-1}$		$^{01}k_{obs}=7.68\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table - 5 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	5.10	0.707	5.02	0.701	5.00	0.699
2	-	-	4.76	0.678	4.72	0.674
3	4.62	0.665	4.38	0.641	4.32	0.635
5	4.04	0.606	3.68	0.566	3.44	0.550
7	-	-	3.00	0.477	2.86	0.456
8	3.30	0.518	-	-	-	-
10	2.86	0.456	2.34	0.369	2.12	0.326
13	2.34	0.369	1.78	0.250	1.62	0.209
15	2.04	0.309	1.52	0.182	1.38	0.139
18	1.68	0.225	1.24	0.093	1.10	0.041
20	1.48	0.170	1.10	0.041	-	-
25	1.04	0.017	-	-	-	-
	$^{01}k_{obs}=11.13\times10^{-4}s^{-1}$		$^{01}k_{obs}=13.42\times10^{-4}s^{-1}$		$^{01}k_{obs}=15.35\times10^{-4}s^{-1}$	

Temp = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}

$[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [surfactants]=Nil.

Table - 6 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	4.80	0.681	4.70	0.672	4.50	0.653
5	4.38	0.641	4.26	0.629	3.92	0.593
8	-	-	3.76	0.575	3.08	0.488
10	3.60	0.556	3.38	0.529	2.64	0.422
13	-	-	2.90	0.462	2.10	0.322
15	2.98	0.474	2.60	0.415	1.78	0.250
18	-	-	2.24	0.350	1.48	0.170
20	2.40	0.380	1.98	0.297	1.28	0.107
23	-	-	-	-	1.08	0.033
25	1.92	0.283	1.54	0.187	-	-
30	1.60	0.204	1.24	0.093	-	-
35	1.30	0.114	-	-	-	-
40	1.06	0.025	-	-	-	-
	$^{01}k_{obs}=6.91\times10^{-4}s^{-1}$		$^{01}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{01}k_{obs}=11.51\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table - 7 : Effect of the concentration of glycine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.80	0.681	4.68	0.670	4.54	0.657
2	4.40	0.643	4.14	0.617	4.06	0.608
3	4.02	0.604	3.60	0.556	3.44	0.536
4	3.60	0.556	3.18	0.502	2.86	0.456
5	3.24	0.510	2.76	0.441	2.46	0.391
6	2.90	0.462	2.40	0.380	2.14	0.330
7	-	-	-	-	1.86	0.269
8	2.34	0.369	1.88	0.274	1.62	0.209
9	-	-	1.66	0.220	1.42	0.152
10	1.90	0.278	1.42	0.152	1.24	0.093
12	1.60	0.204	1.10	0.041	-	-
15	1.26	0.100	-	-	-	-
	$^{01}k_{obs}=17.27\times10^{-4}s^{-1}$		$^{01}k_{obs}=22.39\times10^{-4}s^{-1}$		$^{01}k_{obs}=24.95\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-8 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.20 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724
5	-	-	5.14	0.711
10	4.94	0.694	4.94	0.694
20	4.52	0.655	4.50	0.653
30	4.16	0.619	4.06	0.608
45	3.70	0.568	3.42	0.534
55	-	-	3.10	0.491
60	3.20	0.505	-	-
75	-	-	2.48	0.394
80	2.66	0.425	-	-
100	2.20	0.342	1.90	0.279
120	1.80	0.255	1.52	0.182
140	1.50	0.176	-	-
145	-	-	1.14	0.057
170	1.14	0.057	-	-
	$^{01}k_{obs}=1.14\times10^{-4}s^{-1}$		$^{01}k_{obs}=1.66\times10^{-4}s^{-1}$	

Temp = 30^oC, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-9 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.10 M		0.07 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724
5	5.14	0.711	4.82	0.683
10	4.92	0.692	4.60	0.663
15	4.70	0.672	-	-
20	-	-	4.08	0.611
30	3.92	0.593	3.54	0.549
45	3.22	0.508	2.88	0.459
60	2.66	0.425	2.34	0.369
75	2.22	0.346	1.84	0.265
90	1.86	0.269	1.52	0.182
105	1.52	0.182	1.20	0.079
120	1.34	0.127	1.08	0.033
	$^{01}k_{obs}=1.92\times10^{-4}s^{-1}$		$^{01}k_{obs}=2.30\times10^{-4}s^{-1}$	

Temp = 30^oC, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table - 10 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.06 M		0.05 M		0.04 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.92	0.692	4.86	0.687	4.80	0.681
10	4.66	0.668	4.52	0.655	4.36	0.639
15	-	-	4.20	0.623	3.98	0.599
20	4.08	0.610	3.82	0.582	3.64	0.561
30	3.46	0.539	3.28	0.516	2.98	0.474
40	3.02	0.480	2.84	0.453	2.52	0.401
50	2.60	0.415	2.38	0.376	2.00	0.301
60	2.18	0.338	2.00	0.301	1.68	0.225
70	-	-	-	-	1.40	0.146
75	1.70	0.230	1.56	0.193	-	-
80	-	-	-	-	1.24	0.093
90	1.30	0.114	1.30	0.113	-	-
105	1.04	0.017	-	-	-	-
	$^{01}k_{obs}=2.49\times10^{-4}s^{-1}$		$^{01}k_{obs}=2.68\times10^{-4}s^{-1}$		$^{01}k_{obs}=3.07\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-11 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.03 M		0.02 M		0.01 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
2	-	-	4.86	0.687	-	-
3	4.84	0.685	-	-	-	-
5	4.60	0.663	4.30	0.633	3.98	0.599
10	4.00	0.602	3.48	0.541	2.94	0.468
15	3.54	0.549	2.92	0.465	2.18	0.338
18	-	-	-	-	1.88	0.274
20	-	-	2.56	0.408	1.78	0.250
23	-	-	-	-	1.56	0.193
25	2.76	0.441	2.28	0.358	1.46	0.164
28	-	-	-	-	1.34	0.127
30	2.48	0.394	1.90	0.279	1.18	0.071
35	-	-	1.70	0.230	1.04	0.017
40	1.96	0.292	-	-	-	-
45	-	-	1.30	0.114	-	-
50	1.60	0.204	-	-	-	-
55	-	-	1.08	0.033	-	-
65	1.26	0.100	-	-	-	-
	$^{01}k_{obs}=4.03\times10^{-4}s^{-1}$		$^{01}k_{obs}=5.18\times10^{-4}s^{-1}$		$^{01}k_{obs}=8.83\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-12 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.20 M		0.15 M		0.10 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.96	0.695	5.10	0.707	4.94	0.694
10	4.50	0.653	4.72	0.624	4.60	0.663
15	4.24	0.627	4.30	0.633	4.18	0.621
20	3.92	0.593	3.94	0.595	3.76	0.575
25	3.54	0.549	3.60	0.556	3.38	0.529
35	3.10	0.491	3.04	0.483	2.78	0.444
45	2.64	0.422	2.50	0.398	2.24	0.350
55	-	-	-	-	1.86	0.269
60	2.04	0.309	-	-	-	-
65	-	-	1.76	0.245	1.50	0.176
75	1.60	0.204	1.50	0.176	1.18	0.072
90	1.10	0.041	1.02	0.008	-	-
	$^{01}k_{obs}=2.69\times10^{-4}s^{-1}$		$^{01}k_{obs}=2.89\times10^{-4}s^{-1}$		$^{01}k_{obs}=3.26\times10^{-4}s^{-1}$	

Temp = 35^oC, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-13 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.07 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724
5	5.10	0.707	5.00	0.699
10	4.64	0.666	4.52	0.655
15	4.20	0.623	4.06	0.608
20	3.70	0.568	3.58	0.554
25	3.30	0.518	3.16	0.499
30	-	-	2.80	0.447
35	2.58	0.412	2.44	0.387
40	-	-	2.10	0.322
45	1.96	0.292	-	-
50	-	-	1.60	0.204
55	1.56	0.193	-	-
60	-	-	1.26	0.100
65	1.22	0.086	-	-
	$^{01}k_{obs}=3.84\times10^{-4}s^{-1}$		$^{01}k_{obs}=4.03\times10^{-4}s^{-1}$	

Temp = 35^oC, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-14 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.05 M		0.04 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724
5	4.76	0.678	4.56	0.659
10	4.24	0.627	3.88	0.589
15	3.70	0.568	3.36	0.526
20	3.30	0.518	2.88	0.459
25	2.86	0.456	2.46	0.391
30	2.54	0.404	2.12	0.326
35	-	-	1.84	0.265
40	1.92	0.283	1.60	0.204
45	-	-	1.18	0.072
50	1.44	0.158	-	-
60	1.12	0.049	-	-
	$^{01}k_{obs}=4.22\times10^{-4}s^{-1}$		$^{01}k_{obs}=4.99\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-15 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.20 M		0.15 M		0.10 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.56	0.659	4.52	0.655	4.54	0.657
10	3.92	0.593	3.86	0.586	3.82	0.582
15	3.46	0.539	3.32	0.521	3.18	0.502
20	3.06	0.486	2.86	0.456	2.68	0.428
25	2.72	0.434	2.50	0.397	2.26	0.354
30	2.38	0.376	2.18	0.338	1.90	0.278
35	2.06	0.314	1.90	0.279	1.60	0.204
40	1.78	0.250	1.58	0.199	1.36	0.133
45	1.56	0.193	1.42	0.152	1.16	0.064
50	-	-	1.20	0.079	-	-
55	1.08	0.033	-	-	-	-
	$^{01}k_{obs}=4.60\times10^{-4}s^{-1}$		$^{01}k_{obs}=4.99\times10^{-4}s^{-1}$		$^{01}k_{obs}=5.76\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-16 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.07 M		0.06 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	-	-	4.80	0.681
5	4.56	0.659	4.54	0.657	4.38	0.641
10	3.86	0.586	3.82	0.582	3.64	0.561
15	3.20	0.505	3.14	0.497	2.98	0.474
20	2.54	0.405	2.54	0.405	2.40	0.380
25	2.08	0.318	2.04	0.309	1.92	0.283
30	1.68	0.225	1.64	0.215	1.60	0.204
35	1.34	0.130	1.34	0.127	1.30	0.114
40	1.12	0.049	1.06	0.025	1.04	0.017
	$^{01}k_{obs}=6.39\times10^{-4}s^{-1}$		$^{01}k_{obs}=6.65\times10^{-4}s^{-1}$		$^{01}k_{obs}=6.91\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

Table-17 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

$[H^+]$	0.04 M		0.03 M		0.02 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.72	0.673
3	4.48	0.651	4.22	0.625	3.96	0.598
5	4.00	0.602	3.82	0.582	3.24	0.510
8	3.40	0.531	3.20	0.505	2.62	0.418
10	3.08	0.488	2.88	0.459	2.36	0.373
13	-	-	-	-	1.90	0.270
15	2.40	0.380	2.20	0.342	1.68	0.225
18	-	-	1.92	0.283	1.46	0.164
20	1.94	0.288	1.72	0.235	1.24	0.093
23	-	-	-	-	1.10	0.041
25	1.50	0.176	1.42	0.152	-	-
30	1.24	0.093	1.18	0.072	-	-
35	1.04	0.017	-	-	-	-
	$^{01}k_{obs}=8.18\times10^{-4}s^{-1}$		$^{01}k_{obs}=9.21\times10^{-4}s^{-1}$		$^{01}k_{obs}=12.28\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [surfactants]=Nil.

OXIDATION OF GLYCINE IN THE PRESENCE OF SDS

Tables 18 to 35 : Effect of the concntration of glycine on the observed rate constant ($^{-1}k_{obs}$).

The conditions were kept constant as described earlier in the absence of surfactant to see the effect of the concentration of glycine under the condition that [SDS] > cmc (0.01 to 0.03 moldm^{-3}).

Tables 36 to 41 : Effect of the [H^+] on the observed rate constant ($^{-1}k_{obs}$).

The conditions employed were similar as described for the absence of surfactant to see the effect of the [H^+] under the condition the [SDS] > cmc (0.01 moldm^{-3}).

Table-18 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	5.02	0.701	5.10	0.707	4.90	0.690
10	4.90	0.690	4.94	0.693	4.56	0.659
15	4.72	0.674	4.66	0.668	4.16	0.619
20	4.56	0.659	4.38	0.641	3.76	0.575
25	-	-	-	-	3.38	0.529
30	4.12	0.614	3.86	0.586	3.00	0.477
35	3.92	0.593	-	-	2.72	0.434
45	3.60	0.556	3.02	0.480	2.16	0.334
60	3.06	0.486	2.42	0.384	1.58	0.198
75	2.52	0.401	1.90	0.279	1.24	0.100
90	2.02	0.305	1.54	0.187	-	-
105	-	-	1.08	0.033	-	-
110	1.70	0.230	-	-	-	-
135	1.20	0.086	-	-	-	-
	$^{-1}k_{obs}=1.79\times10^{-4}s^{-1}$		$^{-1}k_{obs}=2.30\times10^{-4}s^{-1}$		$^{-1}k_{obs}=3.45\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-19 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
2	-	-	5.00	0.699	5.00	0.699
5	4.70	0.672	4.74	0.676	4.60	0.662
7	-	-	-	-	4.12	0.614
10	4.10	0.612	3.92	0.593	3.60	0.556
15	3.60	0.556	3.10	0.491	2.80	0.447
20	3.10	0.491	2.56	0.408	2.14	0.330
25	2.62	0.418	2.10	0.322	1.72	0.235
30	2.26	0.354	1.68	0.225	1.40	0.146
35	1.92	0.283	1.44	0.158	1.14	0.057
40	1.64	0.214	1.16	0.064	-	-
50	1.28	0.107	-	-	-	-
60	1.00	0.000	-	-	-	-
	$^{-1}k_{obs}=4.79\times10^{-4}s^{-1}$		$^{-1}k_{obs}=6.14\times10^{-4}s^{-1}$		$^{-1}k_{obs}=7.29\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.01 moldm^{-3}

Table-20 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	-	-	-	-	4.84	0.684
10	-	-	4.86	0.687	4.56	0.659
15	4.68	0.670	-	-	4.24	0.627
20	-	-	4.50	0.653	3.90	0.591
30	4.20	0.623	4.06	0.608	3.24	0.510
45	3.70	0.568	3.36	0.526	2.48	0.394
60	3.12	0.494	2.76	0.441	1.84	0.264
75	2.72	0.434	2.22	0.346	1.48	0.170
90	2.20	0.342	1.86	0.269	1.18	0.072
105	1.90	0.279	1.56	0.193	-	-
120	1.66	0.220	1.32	0.120	-	-
135	1.32	0.120	1.14	0.056	-	-
150	1.20	0.079	-	-	-	-
	$^{-1}k_{obs}=1.53\times10^{-4}s^{-1}$		$^{-1}k_{obs}=2.05\times10^{-4}s^{-1}$		$^{-1}k_{obs}=2.93\times10^{-4}s^{-1}$	

Temp = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.02 moldm^{-3}

Table-21 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.68	0.670	4.74	0.676	4.38	0.641
10	4.18	0.621	4.06	0.608	3.56	0.551
15	3.66	0.563	3.46	0.539	2.86	0.456
20	3.26	0.513	2.84	0.453	2.26	0.354
25	2.80	0.447	2.40	0.380	1.78	0.250
30	2.40	0.380	2.08	0.318	1.50	0.176
35	2.10	0.322	1.74	0.241	1.28	0.107
40	-	-	1.46	0.164	1.08	0.033
45	1.62	0.209	1.26	0.100	-	-
50	-	-	1.16	0.064	-	-
60	1.16	0.064	-	-	-	-
	$^{-1}k_{obs}=4.22\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.37\times10^{-4}s^{-1}$		$^{-1}k_{obs}=6.91\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.02 $moldm^{-3}$

Table-22 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	-	-	-	-	4.86	0.687
10	-	-	-	-	4.60	0.663
15	4.76	0.678	4.68	0.670	4.38	0.641
20	-	-	-	-	4.06	0.608
30	4.26	0.629	4.10	0.613	3.60	0.556
45	3.80	0.579	3.56	0.551	2.66	0.424
60	3.42	0.534	2.96	0.471	2.24	0.350
75	2.90	0.462	2.54	0.404	-	-
80	-	-	-	-	1.72	0.235
90	2.52	0.401	2.14	0.330	-	-
100	-	-	-	-	1.36	0.133
105	2.16	0.334	1.84	0.265	-	-
120	1.90	0.278	1.60	0.204	1.08	0.033
135	-	-	1.36	0.133	-	-
140	1.56	0.193	-	-	-	-
150	-	-	1.22	0.086	-	-
160	1.34	0.127	-	-	-	-
	$^{-1}k_{obs}=1.34\times10^{-4}s^{-1}$		$^{-1}k_{obs}=1.79\times10^{-4}s^{-1}$		$^{-1}k_{obs}=2.43\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.03 $moldm^{-3}$

Table-23 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	-	-	4.86	0.687
5	4.84	0.684	4.84	0.684	4.56	0.659
10	4.46	0.649	4.24	0.627	4.02	0.604
15	3.98	0.599	3.64	0.561	3.34	0.523
20	3.56	0.551	3.28	0.488	2.64	0.421
25	-	-	2.70	0.431	2.24	0.350
30	2.80	0.447	2.26	0.354	1.82	0.260
35	2.50	0.398	1.88	0.274	1.54	0.187
40	-	-	1.68	0.225	1.34	0.127
45	2.00	0.301	-	-	1.20	0.079
50	-	-	1.26	0.100	-	-
60	1.62	0.209	1.10	0.041	-	-
75	1.16	0.064	-	-	-	-
	$^{-1}k_{obs}=3.65\times10^{-4}s^{-1}$		$^{-1}k_{obs}=4.60\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.76\times10^{-4}s^{-1}$	

Temp = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.03 moldm^{-3}

Table-24 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	5.00	0.699	4.92	0.692	4.72	0.678
10	4.72	0.673	4.54	0.657	4.12	0.615
15	-	-	4.04	0.606	3.44	0.536
20	4.08	0.610	3.66	0.563	2.86	0.456
25	-	-	3.20	0.505	2.38	0.376
30	3.50	0.544	-	-	2.00	0.301
35	-	-	2.48	0.394	1.66	0.220
40	2.94	0.468	-	-	1.38	0.139
45	-	-	1.90	0.279	1.20	0.079
50	2.40	0.380	-	-	-	-
55	-	-	1.50	0.176	-	-
60	1.94	0.287	-	-	-	-
65	-	-	1.20	0.079	-	-
70	1.66	0.220	-	-	-	-
80	1.34	0.127	-	-	-	-
80	1.16	0.064	-	-	-	-
	$^{-1}k_{obs}=2.81\times10^{-4}s^{-1}$		$^{-1}k_{obs}=3.67\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.76\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-25 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	5.06	0.704
3	4.80	0.681	4.68	0.670	4.56	0.659
5	4.40	0.643	4.14	0.617	3.94	0.595
8	3.84	0.584	3.40	0.531	3.06	0.485
10	3.44	0.536	2.94	0.468	2.54	0.405
13	2.90	0.462	2.38	0.376	2.00	0.301
15	2.58	0.412	2.12	0.326	1.70	0.230
18	-	-	1.68	0.225	1.40	1.46
20	1.96	0.292	1.52	0.182	1.20	0.079
23	-	-	1.24	0.093	-	-
25	1.54	0.187	1.06	0.025	-	-
30	1.22	0.086	-	-	-	-
35	1.02	0.009	-	-	-	-
	$^{-1}k_{obs}=8.06\times10^{-4}s^{-1}$		$^{-1}k_{obs}=10.36\times10^{-4}s^{-1}$		$^{-1}k_{obs}=12.47\times10^{-4}s^{-1}$	

Temp = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.01 moldm^{-3}

Table-26 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.82	0.683	4.78	0.679	4.72	0.674
10	4.66	0.668	4.46	0.649	4.20	0.623
15	-	-	-	-	3.62	0.559
20	4.06	0.608	4.14	0.617	3.12	0.494
25	-	-	3.38	0.529	2.70	0.431
30	3.46	0.539	-	-	2.30	0.361
35	-	-	2.70	0.431	1.98	0.297
40	2.88	0.459	-	-	1.72	0.235
45	-	-	2.20	0.342	-	-
50	2.42	0.384	-	-	1.36	0.133
55	-	-	1.82	0.260	-	-
60	2.00	0.301	-	-	1.08	0.033
65	-	-	1.46	0.164	-	-
70	1.64	0.215	-	-	-	-
75	-	-	1.26	0.100	-	-
80	1.36	0.133	-	-	-	-
85	-	-	1.04	0.017	-	-
90	1.16	0.064	-	-	-	-
	$^{-1}k_{obs}=2.69\times10^{-4}s^{-1}$		$^{-1}k_{obs}=3.26\times10^{-4}s^{-1}$		$^{-1}k_{obs}=4.60\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, $[H^{+}] = 0.05$ moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.02 moldm^{-3}

Table-27 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	4.88	0.688	4.62	0.665	4.66	0.668
5	4.60	0.663	4.28	0.631	4.16	0.619
8	-	-	3.56	0.551	3.34	0.524
10	3.78	0.577	3.16	0.499	2.94	0.468
13	-	-	2.72	0.434	2.34	0.369
15	3.08	0.488	2.38	0.376	2.06	0.314
18	-	-	1.98	0.297	1.74	0.240
20	2.40	0.380	1.78	0.250	1.50	0.176
23	-	-	1.64	0.215	1.28	0.107
25	2.00	0.301	-	-	1.14	0.057
30	1.62	0.209	1.22	0.086	-	-
35	1.24	0.093	-	-	-	-
40	1.10	0.041	-	-	-	-
	$^{-1}k_{obs}=6.52\times10^{-4}s^{-1}$		$^{-1}k_{obs}=8.83\times10^{-4}s^{-1}$		$^{-1}k_{obs}=10.36\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.02 $moldm^{-3}$

Table-28 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	-	-	-	-	4.54	0.657
10	4.60	0.663	4.40	0.643	4.18	0.621
15	-	-	-	-	3.66	0.563
20	4.14	0.617	3.86	0.586	3.24	0.510
25	-	-	-	-	2.84	0.453
30	3.62	0.559	3.20	0.505	2.50	0.398
40	3.16	0.499	2.68	0.428	1.98	0.297
50	2.64	0.422	2.26	0.354	1.60	0.204
60	2.26	0.354	1.90	0.279	1.32	0.120
70	1.88	0.274	1.62	0.209	1.06	0.025
80	1.62	0.209	1.38	0.139	-	-
90	1.40	0.146	1.22	0.086	-	-
100	-	-	1.08	0.033	-	-
105	1.02	0.009	-	-	-	-
	$^{-1}k_{obs}=2.30\times10^{-4}s^{-1}$		$^{-1}k_{obs}=2.88\times10^{-4}s^{-1}$		$^{-1}k_{obs}=4.03\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.03 $moldm^{-3}$

Table-29 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	4.74	0.676	4.72	0.674
5	4.56	0.659	4.42	0.645	4.24	0.627
8	-	-	3.82	0.582	3.56	0.551
10	3.84	0.584	3.44	0.536	3.14	0.497
13	-	-	-	-	2.66	0.425
15	3.22	0.508	2.66	0.425	2.28	0.358
20	2.66	0.425	2.14	0.330	1.76	0.245
25	2.20	0.342	1.66	0.220	1.36	0.133
30	1.88	0.274	1.36	0.133	1.06	0.025
35	1.58	0.199	1.08	0.033	-	-
40	1.36	0.133	-	-	-	-
45	1.20	0.079	-	-	-	-
50	1.10	0.041	-	-	-	-
	$^{-1}k_{obs}=5.37\times10^{-4}s^{-1}$		$^{-1}k_{obs}=7.68\times10^{-4}s^{-1}$		$^{-1}k_{obs}=8.83\times10^{-4}s^{-1}$	

Temp = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.03 moldm^{-3}

Table-30 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
3	-	-	5.06	0.704	4.70	0.672
5	4.86	0.687	4.90	0.690	4.32	0.635
8	-	-	4.50	0.653	3.76	0.575
10	4.32	0.635	4.20	0.623	3.34	0.524
13	-	-	-	-	2.88	0.459
15	3.76	0.575	3.58	0.554	2.58	0.412
18	-	-	-	-	2.18	0.338
20	3.22	0.508	2.90	0.462	1.94	0.288
25	2.72	0.434	2.36	0.373	1.50	0.176
30	2.30	0.362	1.94	0.288	1.24	0.093
35	1.88	0.274	1.60	0.204	-	-
40	1.62	0.209	1.26	0.100	-	-
45	1.30	0.113	-	-	-	-
50	1.10	0.041	-	-	-	-
	$^{-1}k_{obs}=5.12\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.88\times10^{-4}s^{-1}$		$^{-1}k_{obs}=8.44\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-31 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
1	5.00	0.699	4.78	0.679	4.82	0.683
2	-	-	4.44	0.647	4.40	0.643
3	4.56	0.659	4.10	0.613	3.96	0.597
4	-	-	3.62	0.559	3.46	0.539
5	4.00	0.602	-	-	3.00	0.477
6	-	-	2.98	0.474	2.66	0.425
8	3.16	0.499	2.44	0.387	2.08	0.318
10	2.72	0.434	1.96	0.292	1.70	0.230
12	-	-	1.62	0.209	1.38	0.139
13	2.16	0.334	-	-	-	-
15	1.86	0.269	1.28	0.107	1.08	0.033
18	1.50	0.176	-	-	-	-
20	1.30	0.114	1.00	0.000	-	-
23	1.12	0.049	-	-	-	-
	$^{-1}k_{obs}=11.89\times10^{-4}s^{-1}$		$^{-1}k_{obs}=15.99\times10^{-4}s^{-1}$		$^{-1}k_{obs}=18.55\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-32 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
3	-	-	4.94	0.694	4.84	0.685
5	4.84	0.685	4.78	0.679	4.56	0.659
8	-	-	-	-	4.06	0.608
10	4.34	0.637	4.08	0.611	3.66	0.563
15	3.90	0.591	3.64	0.561	3.10	0.490
20	3.42	0.534	3.12	0.494	2.48	0.394
25	2.92	0.465	2.66	0.425	1.90	0.278
30	2.60	0.415	2.26	0.354	1.70	0.230
35	2.18	0.338	1.94	0.287	1.32	0.120
40	1.86	0.269	1.64	0.215	1.12	0.049
50	1.40	0.146	1.26	0.100	-	-
60	1.08	0.033	-	-	-	-
	$^{-1}k_{obs}=4.09\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.15\times10^{-4}s^{-1}$		$^{-1}k_{obs}=6.65\times10^{-4}s^{-1}$	

Temp = 40°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2 X 10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u = 0.20 moldm^{-3} [SDS]=0.02 moldm^{-3}

Table-33 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
1	-	-	-	-	5.00	0.699
2	-	-	-	-	4.72	0.674
3	4.80	0.681	4.58	0.661	4.32	0.635
4	-	-	-	-	3.90	0.591
5	4.26	0.629	3.88	0.589	3.40	0.531
6	-	-	-	-	3.20	0.505
8	3.54	0.549	3.00	0.477	2.56	0.408
10	3.08	0.488	2.50	0.398	2.10	0.322
12	-	-	-	-	1.70	0.230
13	2.60	0.415	1.98	0.297	-	-
15	2.30	0.362	1.72	0.235	1.26	0.100
18	1.92	0.283	1.36	0.133	-	-
20	1.70	0.230	1.22	0.086	-	-
23	-	-	1.00	0.000	-	-
25	1.30	0.114	-	-	-	-
30	1.00	0.000	-	-	-	-
	$^{-1}k_{obs}=9.98\times10^{-4}s^{-1}$		$^{-1}k_{obs}=12.79\times10^{-4}s^{-1}$		$^{-1}k_{obs}=15.35\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.02 $moldm^{-3}$

Table-34 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
5	4.92	0.692	4.80	0.681	4.62	0.665
10	4.52	0.655	4.38	0.641	3.82	0.582
15	4.06	0.608	3.84	0.584	3.18	0.502
20	3.68	0.566	3.34	0.524	2.68	0.428
25	-	-	2.94	0.468	2.18	0.338
30	2.88	0.459	2.60	0.415	1.92	0.283
35	-	-	2.24	0.350	1.58	0.198
40	2.18	0.338	-	-	1.36	0.133
45	-	-	1.74	0.240	1.20	0.079
50	1.68	0.225	-	-	1.08	0.033
55	-	-	1.40	0.146	-	-
60	1.34	0.127	-	-	-	-
65	-	-	1.16	0.064	-	-
70	1.06	0.025	-	-	-	-
	$^{-1}k_{obs}=3.65\times10^{-4}s^{-1}$		$^{-1}k_{obs}=4.22\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.56\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.03 $moldm^{-3}$

Table-35 : Effect of the concentration of glycine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
1	-	-	-	-	4.86	0.687
2	-	-	-	-	4.68	0.670
3	4.66	0.668	4.72	0.674	4.30	0.633
4	-	-	-	-	3.96	0.598
5	4.24	0.627	4.06	0.608	-	-
6	-	-	-	-	3.34	0.524
8	3.64	0.561	3.30	0.518	2.78	0.444
10	3.24	0.516	2.82	0.450	2.30	0.362
12	-	-	-	-	1.88	0.274
13	2.74	0.438	2.24	0.350	-	-
15	2.50	0.398	1.96	0.292	1.58	0.198
18	-	-	1.64	0.215	-	-
20	1.90	0.279	1.44	0.158	1.10	0.041
23	-	-	1.18	0.072	-	-
25	1.50	0.176	-	-	-	-
30	1.20	0.079	-	-	-	-
35	1.00	0.000	-	-	-	-
	$^{-1}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{-1}k_{obs}=10.75\times10^{-4}s^{-1}$		$^{-1}k_{obs}=12.79\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.03 $moldm^{-3}$

Table-36 : Effect of the $[H^+]$ on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

$[H^+]$	0.05 M		0.04 M		0.03 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
5	5.02	0.701	4.96	0.695	4.92	0.692
10	4.90	0.690	-	-	4.70	0.672
15	4.72	0.574	4.70	0.672	4.38	0.641
20	4.56	0.659	-	-	-	-
25	-	-	4.30	0.633	3.78	0.577
30	4.12	0.612	-	-	-	-
35	3.92	0.593	3.80	0.579	3.30	0.518
45	3.60	0.556	3.40	0.531	2.80	0.447
60	3.06	0.486	2.80	0.447	2.24	0.350
75	2.52	0.401	2.30	0.362	1.82	0.260
90	2.02	0.305	1.90	0.278	-	-
100	-	-	-	-	1.32	0.120
110	1.70	0.230	1.50	0.176	-	-
120	-	-	-	-	1.20	0.079
130	-	-	1.24	0.093	-	-
135	1.22	0.086	-	-	-	-
	$^{-1}k_{obs}=1.79\times10^{-4}s^{-1}$		$^{-1}k_{obs}=1.92\times10^{-4}s^{-1}$		$^{-1}k_{obs}=2.43\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-37 : Effect of the $[H^+]$ on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

$[H^+]$	0.02 M		0.01 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729
2	-	-	4.84	0.685
5	4.60	0.663	4.18	0.621
10	4.10	0.613	3.20	0.505
15	3.64	0.561	2.60	0.415
20	3.20	0.505	2.04	0.309
25	2.90	0.462	1.72	0.235
30	-	-	1.40	0.146
35	2.46	0.391	1.20	0.079
40	-	-	1.06	0.025
50	1.78	0.250	-	-
60	1.46	0.164	-	-
70	1.20	0.079	-	-
80	1.00	0.000	-	-
	$^{-1}k_{obs}=3.84\times10^{-4}s^{-1}$		$^{-1}k_{obs}=7.67\times10^{-4}s^{-1}$	

Temp = $30^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-38 : Effect of the $[H^+]$ on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

$[H^+]$	0.05 M		0.04 M		0.03 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729	5.36	0.729
5	5.00	0.699	5.00	0.699	4.86	0.687
10	4.72	0.672	4.60	0.663	4.42	0.645
15	-	-	-	-	3.98	0.599
20	4.10	0.613	4.00	0.602	3.54	0.549
25	-	-	-	-	3.20	0.505
30	3.50	0.544	3.38	0.528	2.80	0.447
35	-	-	-	-	2.52	0.401
40	2.94	0.468	2.74	0.438	-	-
45	-	-	-	-	2.00	0.301
50	2.40	0.380	2.22	0.346	-	-
60	1.94	0.287	1.82	0.260	1.50	0.176
70	1.66	0.220	1.50	0.176	-	-
75	-	-	-	-	1.16	0.064
80	1.34	0.127	1.28	0.107	-	-
90	1.16	0.064	1.04	0.017	-	-
	$^{-1}k_{obs}=2.81\times10^{-4}s^{-1}$		$^{-1}k_{obs}=3.07\times10^{-4}s^{-1}$		$^{-1}k_{obs}=3.64\times10^{-4}s^{-1}$	

Temp = 35^oC, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-39 : Effect of the $[H^+]$ on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

$[H^+]$	0.02 M		0.01 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729
3	4.96	0.695	4.40	0.643
5	4.68	0.670	3.86	0.586
8	4.20	0.623	3.06	0.486
10	3.94	0.595	2.70	0.431
13	-	-	2.28	0.358
15	3.28	0.516	2.04	0.309
18	-	-	1.80	0.255
20	2.80	0.447	1.66	0.220
25	2.40	0.380	1.38	0.139
30	2.08	0.318	1.20	0.079
40	1.58	0.198	-	-
50	1.22	0.086	-	-
	$^{-1}k_{obs}=5.18\times10^{-4}s^{-1}$		$^{-1}k_{obs}=10.36\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-40 : Effect of the $[H^+]$ on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

$[H^+]$	0.05 M		0.04 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729
3	-	-	4.56	0.659
5	4.86	0.687	4.40	0.643
10	4.32	0.635	3.90	0.591
15	3.76	0.575	3.32	0.521
20	3.22	0.508	2.82	0.450
25	2.72	0.434	2.40	0.380
30	2.30	0.362	2.04	0.309
35	1.88	0.275	1.72	0.235
40	1.62	0.209	1.50	0.176
45	1.30	0.113	-	-
50	1.10	0.041	1.16	0.064
	$^{-1}k_{obs}=5.12\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.37\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS]=0.01 $moldm^{-3}$

Table-41 : Effect of the $[H^+]$ on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

$[H^+]$	0.03 M		0.02 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.36	0.729	5.36	0.729
3	4.46	0.649	4.28	0.631
5	4.18	0.621	3.82	0.582
8	3.80	0.579	3.20	0.505
10	3.50	0.544	2.86	0.456
13	-	-	2.42	0.384
15	2.90	0.462	2.16	0.334
18	-	-	1.88	0.274
20	2.42	0.384	1.70	0.230
25	2.00	0.301	1.38	0.139
30	1.72	0.235	1.16	0.064
35	1.46	0.164	-	-
40	1.24	0.093	-	-
	$^{-1}k_{obs}=6.65\times10^{-4}s^{-1}$		$^{-1}k_{obs}=8.18\times10^{-4}s^{-1}$	

Temp = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [SDS] = 0.01 $moldm^{-3}$

OXIDATION OF GLYCINE IN THE PRESENCE OF CPC

Tables 42 to 59 : Effect of the concentration of glycine on the observed Rate constant ($^{+1}k_{obs}$)

The conditions were kept constant as described earlier in the absence of surfactant to see the effect of the concentration of glycine under the conditions that [CPC] > cmc (0.002, 0.004 and 0.006 moldm^{-3}).

Tables 60 to 66 : Effect of the [H^+] on the observed rate constant ($^{+1}k_{obs}$).

The conditions employed were similar as described for the absence of surfactant to see the effect of the [H^+] under the conditions that [CPC] > cms (0.004 moldm^{-3}).

Table 42 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	5.12	0.709	4.92	0.692	4.84	0.685
10	4.86	0.687	4.58	0.661	4.28	0.631
15	4.44	0.647	3.96	0.597	3.52	0.546
20	4.06	0.608	3.60	0.556	3.00	0.477
25	-	-	3.20	0.505	2.56	0.408
30	3.40	0.531	2.90	0.462	2.10	0.322
35	-	-	-	-	1.86	0.269
40	2.86	0.456	2.24	0.350	1.58	0.198
45	-	-	-	-	1.36	0.133
50	2.40	0.380	1.76	0.246	1.10	0.041
60	2.00	0.301	1.38	0.139	-	-
70	-	-	1.12	0.049	-	-
75	1.56	0.193	-	-	-	-
90	1.10	0.041	-	-	-	-
	$^{+1}k_{obs}=2.94\times10^{-4}s^{-1}$		$^{+1}k_{obs}=3.71\times10^{-4}s^{-1}$		$^{+1}k_{obs}=5.12\times10^{-4}s^{-1}$	

Temp. = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.002 moldm^{-3}.

Table 43 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	4.74	0.675	4.80	0.681	4.58	0.660
5	4.36	0.639	4.50	0.653	4.02	0.604
8	3.70	0.568	3.66	0.563	3.26	0.513
10	3.34	0.523	3.30	0.518	2.80	0.447
13	2.94	0.468	2.80	0.447	2.42	0.384
15	2.60	0.415	2.48	0.394	2.08	0.318
18	-	-	-	-	1.76	0.246
20	2.08	0.318	1.90	0.278	1.64	0.215
25	1.66	0.220	1.46	0.164	1.28	0.107
30	1.38	0.139	1.16	0.064	-	-
35	1.10	0.041	-	-	-	-
	$^{+1}k_{obs}=7.29\times10^{-4}s^{-1}$		$^{+1}k_{obs}=8.82\times10^{-4}s^{-1}$		$^{+1}k_{obs}=10.36\times10^{-4}s^{-1}$	

Temp. = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.002 moldm^{-3}.

Table 44 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	-	-	4.78	0.679
5	4.64	0.66	4.72	0.674	4.46	0.649
8	-	-	-	-	3.88	0.589
10	4.30	0.633	4.20	0.623	3.52	0.546
15	3.74	0.572	3.60	0.556	2.92	0.465
20	3.44	0.536	3.16	0.499	2.40	0.380
25	-	-	2.78	0.444	1.98	0.297
30	2.84	0.453	2.44	0.387	1.58	0.198
35	-	-	2.08	0.318	1.36	0.133
40	2.26	0.354	1.82	0.260	1.12	0.049
50	1.90	0.278	1.38	0.139	-	-
60	1.50	0.176	1.02	0.008	-	-
70	1.20	0.079	-	-	-	-
	$^{+1}k_{obs}=3.45\times10^{-4}s^{-1}$		$^{+1}k_{obs}=4.48\times10^{-4}s^{-1}$		$^{+1}k_{obs}=6.91\times10^{-4}s^{-1}$	

Temp. = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC] = 0.004 moldm^{-3}.

Table 45 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.84	0.685
2	-	-	-	-	4.38	0.641
3	4.40	0.643	4.20	0.623	3.96	0.597
5	3.74	0.572	3.70	0.568	3.20	0.505
8	3.24	0.510	2.78	0.444	2.42	0.384
10	2.90	0.462	2.44	0.387	2.10	0.322
13	2.48	0.394	1.96	0.292	1.66	0.220
15	2.22	0.346	1.74	0.240	1.46	0.164
18	1.86	0.269	1.46	0.164	1.20	0.079
20	1.72	0.235	1.26	0.100	1.06	0.025
23	-	-	1.12	0.049	-	-
25	1.32	0.120	-	-	-	-
30	1.06	0.025	-	-	-	-
	$^{+1}k_{obs}=9.59\times10^{-4}s^{-1}$		$^{+1}k_{obs}=12.66\times10^{-4}s^{-1}$		$^{+1}k_{obs}=15.33\times10^{-4}s^{-1}$	

Temp.= 30^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC] = 0.004 moldm^{-3}.

Table 46 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.88	0.688
3	-	-	-	-	4.10	0.613
5	4.40	0.643	4.10	0.613	3.56	0.551
8	-	-	-	-	2.92	0.465
10	3.86	0.586	3.36	0.526	2.66	0.425
13	-	-	-	-	2.20	0.342
15	3.32	0.521	2.80	0.447	1.96	0.292
18	-	-	-	-	1.64	0.215
20	3.00	0.477	2.32	0.365	1.46	0.164
25	2.60	0.415	1.96	0.292	1.08	0.033
30	2.32	0.365	1.60	0.204	-	-
35	2.00	0.301	1.30	0.113	-	-
40	1.70	0.230	1.10	0.041	-	-
45	1.60	0.204	-	-	-	-
60	1.00	0.000	-	-	-	-
	$^{+1}k_{obs}=4.79\times10^{-4}s^{-1}$		$^{+1}k_{obs}=6.65\times10^{-4}s^{-1}$		$^{+1}k_{obs}=11.89\times10^{-4}s^{-1}$	

Temp.= 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC] = 0.006 moldm^{-3}.

Table 47 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.88	0.688	4.66	0.668	4.52	0.655
2	4.28	0.631	3.94	0.595	3.66	0.563
3	3.90	0.591	3.32	0.521	3.06	0.486
4	-	-	3.00	0.477	2.70	0.431
5	3.10	0.491	2.48	0.394	2.22	0.346
6	-	-	2.10	0.322	2.04	0.309
7	-	-	-	-	1.80	0.255
8	2.32	0.365	1.66	0.220	1.64	0.215
10	1.98	0.297	1.30	0.114	1.42	0.152
12	-	-	1.10	0.041	1.02	0.008
13	1.60	0.204	-	-	-	-
15	1.46	0.164	1.00	0.000	-	-
18	1.12	0.049	-	-	-	-
20	1.00	0.000	-	-	-	-
	$^{+1}k_{obs}=16.63\times10^{-4}s^{-1}$		$^{+1}k_{obs}=23.03\times10^{-4}s^{-1}$		$^{+1}k_{obs}=26.87\times10^{-4}s^{-1}$	

Temp.= 30^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC] = 0.006 moldm^{-3}.

Table 48 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	-	-	4.62	0.665
5	4.80	0.681	4.66	0.668	4.32	0.635
8	-	-	-	-	3.70	0.568
10	4.38	0.641	4.10	0.613	3.30	0.518
13	-	-	-	-	2.78	0.444
15	3.94	0.595	3.52	0.546	2.52	0.401
20	3.54	0.549	2.90	0.462	1.90	0.278
25	3.06	0.486	2.40	0.380	1.52	0.182
30	2.80	0.447	2.10	0.322	1.18	0.072
35	2.44	0.387	1.64	0.215	-	-
40	2.12	0.326	1.36	0.133	-	-
45	-	-	1.16	0.064	-	-
50	1.60	0.204	-	-	-	-
60	1.20	0.079	-	-	-	-
	$^{+1}k_{obs}=4.03\times10^{-4}s^{-1}$		$^{+1}k_{obs}=5.37\times10^{-4}s^{-1}$		$^{+1}k_{obs}=8.83\times10^{-4}s^{-1}$	

Temp.= 35^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC] = 0.002 moldm^{-3}.

Table 49 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	5.00	0.699	4.74	0.676	4.80	0.681
2	-	-	4.44	0.647	4.62	0.665
3	4.48	0.651	-	-	4.20	0.623
4	-	-	3.74	0.573	3.66	0.563
5	3.92	0.593	-	-	3.38	0.529
6	-	-	3.06	0.488	2.78	0.444
8	3.20	0.505	2.50	0.398	2.30	0.361
10	2.70	0.431	2.06	0.314	1.86	0.269
12	-	-	1.78	0.250	-	-
13	2.22	0.346	-	-	1.40	0.146
15	1.88	0.274	1.32	0.120	1.16	0.064
18	-	-	1.12	0.049	-	-
20	1.36	0.133	-	-	-	-
25	1.02	0.008	-	-	-	-
	$^{+1}k_{obs}=11.89\times10^{-4}s^{-1}$		$^{+1}k_{obs}=15.35\times10^{-4}s^{-1}$		$^{+1}k_{obs}=17.27\times10^{-4}s^{-1}$	

Temp. = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.002 moldm^{-3}.

Table 50 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	4.62	0.665	4.12	0.615
5	4.10	0.612	4.04	0.606	3.56	0.551
8	-	-	3.66	0.563	2.84	0.453
10	3.60	0.556	3.33	0.522	-	-
11	-	-	-	-	2.40	0.380
13	-	-	-	-	2.04	0.309
15	3.16	0.499	2.62	0.418	1.78	0.250
18	-	-	-	-	1.46	0.164
20	2.68	0.428	2.08	0.318	1.30	0.113
23	-	-	-	-	1.04	0.017
25	2.32	0.365	1.60	0.204	-	-
30	2.08	0.318	1.34	0.127	-	-
35	1.70	0.230	1.04	0.017	-	-
40	1.50	0.176	-	-	-	-
45	1.18	0.072	-	-	-	-
50	1.00	0.000	-	-	-	-
	$^{+1}k_{obs}=5.75\times10^{-4}s^{-1}$		$^{+1}k_{obs}=7.67\times10^{-4}s^{-1}$		$^{+1}k_{obs}=11.89\times10^{-4}s^{-1}$	

Temp. = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.004 moldm^{-3}.

Table 51 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.52	0.655	4.56	0.659	4.58	0.661
2	-	-	4.08	0.611	3.90	0.591
3	3.60	0.556	3.58	0.554	3.20	0.505
4	-	-	3.14	0.496	2.86	0.456
5	2.88	0.459	2.70	0.431	2.30	0.362
6	-	-	2.34	0.369	2.20	0.342
7	-	-	-	-	1.84	0.265
8	2.18	0.338	1.84	0.265	1.60	0.204
10	1.80	0.255	1.40	0.146	1.26	0.100
13	1.36	0.133	1.16	0.064	-	-
15	1.14	0.056	-	-	-	-
	$^{+1}k_{obs}=16.31\times10^{-4}s^{-1}$		$^{+1}k_{obs}=22.07\times10^{-4}s^{-1}$		$^{+1}k_{obs}=23.99\times10^{-4}s^{-}$	

Temp. = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.004 moldm^{-3}.

Table 52 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.54	0.657
2	-	-	-	-	3.94	0.595
3	4.44	0.647	4.00	0.602	3.40	0.531
4	-	-	-	-	2.84	0.453
5	4.06	0.608	3.50	0.544	2.64	0.422
6	-	-	-	-	2.40	0.380
8	3.46	0.539	2.74	0.438	1.98	0.297
10	3.18	0.502	2.40	0.380	1.60	0.204
13	-	-	1.98	0.297	1.14	0.057
15	2.60	0.415	1.78	0.250	-	-
18	-	-	1.40	0.146	-	-
20	2.22	0.346	1.24	0.093	-	-
25	1.80	0.255	-	-	-	-
30	1.46	0.164	-	-	-	-
35	1.16	0.064	-	-	-	-
	$^{+1}k_{obs}=7.67\times10^{-4}s^{-1}$		$^{+1}k_{obs}=13.05\times10^{-4}s^{-1}$		$^{+1}k_{obs}=22.07\times10^{-4}s^{-1}$	

Temp. = 35°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.006 moldm^{-3}.

Table 53 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.38	0.641	4.12	0.612	4.02	0.604
2	3.38	0.529	3.08	0.488	2.86	0.456
3	2.80	0.447	2.52	0.401	2.16	0.334
4	2.48	0.394	2.00	0.301	1.70	0.230
5	2.04	0.309	1.72	0.235	1.48	0.170
6	1.80	0.255	1.54	0.187	1.26	0.100
7	1.60	0.204	1.24	0.093	1.10	0.041
8	1.30	0.113	1.12	0.049	-	-
9	1.14	0.056	-	-	-	-
10	1.02	0.008	-	-	-	-
	$^{+1}k_{obs}=29.43\times10^{-4}s^{-1}$		$^{+1}k_{obs}=35.50\times10^{-4}s^{-1}$		$^{+1}k_{obs}=44.14\times10^{-4}s^{-1}$	

Temp. = 35^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.006 moldm^{-3}.

Table 54 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.90	0.690
2	-	-	-	-	4.62	0.665
3	4.76	0.678	4.76	0.677	4.40	0.643
5	4.50	0.653	4.48	0.651	3.70	0.568
8	-	-	3.86	0.586	2.96	0.471
10	3.80	0.579	3.40	0.531	2.60	0.415
13	-	-	2.76	0.441	2.00	0.301
15	3.12	0.494	2.50	0.398	1.68	0.225
18	-	-	2.20	0.342	1.30	0.114
20	2.50	0.398	1.84	0.265	1.22	0.086
25	2.00	0.301	1.40	0.146	-	-
30	1.62	0.209	1.04	0.017	-	-
35	1.28	0.107	-	-	-	-
	$^{+1}k_{obs}=6.65\times10^{-4}s^{-1}$		$^{+1}k_{obs}=8.70\times10^{-4}s^{-1}$		$^{+1}k_{obs}=13.05\times10^{-4}s^{-1}$	

Temp. = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.002 $moldm^{-3}$.

Table 55 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.86	0.687	4.62	0.665	4.62	0.665
2	4.46	0.649	4.30	0.633	4.08	0.611
3	3.98	0.599	3.60	0.556	3.40	0.531
4	3.64	0.561	3.10	0.491	2.80	0.447
5	-	-	2.70	0.431	2.38	0.376
6	2.82	0.450	2.40	0.380	2.06	0.314
7	-	-	2.06	0.314	1.72	0.240
8	2.24	0.350	1.76	0.245	1.50	0.176
9	-	-	1.56	0.193	1.30	0.139
10	1.78	0.250	1.40	0.146	-	-
13	1.30	0.114	-	-	-	-
15	1.04	0.017	-	-	-	-
	$^{+1}k_{obs}=17.91\times10^{-4}s^{-1}$		$^{+1}k_{obs}=23.03\times10^{-4}s^{-1}$		$^{+1}k_{obs}=26.87\times10^{-4}s^{-1}$	

Temp. = 40^{O}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.002 moldm^{-3}.

Table 56 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.74	0.676
2	-	-	-	-	4.36	0.639
3	4.48	0.651	4.24	0.627	4.00	0.602
4	-	-	-	-	3.40	0.531
5	4.10	0.612	3.72	0.570	3.10	0.491
6	-	-	-	-	2.80	0.447
8	3.54	0.549	3.06	0.486	2.28	0.358
10	3.24	0.510	2.64	0.421	1.80	0.255
13	2.80	0.447	2.06	0.316	1.36	0.133
15	2.50	0.398	1.80	0.255	1.04	0.017
18	-	-	1.42	0.152	-	-
20	1.96	0.292	1.30	0.114	-	-
23	-	-	1.02	0.008	-	-
25	1.52	0.182	-	-	-	-
30	1.16	0.064	-	-	-	-
	$^{+1}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{+1}k_{obs}=12.28\times10^{-4}s^{-1}$		$^{+1}k_{obs}=17.91\times10^{-4}s^{-1}$	

Temp. = 40°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.004 moldm^{-3}.

Table 57 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.48	0.651	4.32	0.635	4.46	0.649
2	3.94	0.595	3.58	0.554	3.44	0.536
3	3.40	0.531	3.00	0.477	2.72	0.434
4	2.92	0.465	2.40	0.380	2.18	0.338
5	2.56	0.408	2.00	0.301	1.72	0.235
6	2.16	0.334	1.72	0.235	1.50	0.176
7	1.76	0.245	1.44	0.158	1.26	0.100
8	1.62	0.209	1.20	0.079	1.10	0.041
9	-	-	1.10	0.041	-	-
10	1.28	0.107	-	-	-	-
12	1.02	0.008	-	-	-	-
	$^{+1}k_{obs}=23.03\times10^{-4}s^{-1}$		$^{+1}k_{obs}=30.70\times10^{-4}s^{-1}$		$^{+1}k_{obs}=34.50\times10^{-4}s^{-1}$	

Temp. = 40°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.004 moldm^{-3}.

Table 58 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.03 M		0.04 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.48	0.651	4.20	0.623
2	-	-	4.00	0.602	3.42	0.534
3	4.16	0.619	3.60	0.556	2.64	0.422
4	-	-	3.18	0.502	2.26	0.354
5	3.66	0.563	2.86	0.456	1.74	0.240
6	-	-	2.50	0.398	1.52	0.182
7	-	-	-	-	1.30	0.113
8	3.00	0.477	2.06	0.314	-	-
10	2.68	0.428	1.66	0.220	-	-
13	2.16	0.334	1.20	0.079	-	-
15	1.80	0.255	-	-	-	-
18	1.40	0.146	-	-	-	-
20	1.28	0.107	-	-	-	-
23	1.08	0.033	-	-	-	-
	$^{+1}k_{obs}=12.28\times10^{-4}s^{-1}$		$^{+1}k_{obs}=20.47\times10^{-4}s^{-1}$		$^{+1}k_{obs}=35.82\times10^{-4}s^{-1}$	

Temp. = 40°C, $[H^+]$ = 0.05 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.006 $moldm^{-3}$.

Table 59 : Effect of the concentration of glycine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Gly]	0.08 M		0.10 M		0.12 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	3.84	0.584	3.52	0.546	3.36	0.526
2	3.00	0.477	2.56	0.408	2.42	0.384
3	2.30	0.362	1.88	0.274	1.74	0.240
4	1.96	0.292	1.50	0.176	1.38	0.139
5	1.60	0.204	1.24	0.100	1.10	0.041
6	1.32	0.120	1.04	0.017	-	-
7	1.14	0.057	-	-	-	-
	$^{+1}k_{obs}=40.94\times10^{-4}s^{-1}$		$^{+1}k_{obs}=55.65\times10^{-4}s^{-1}$		$^{+1}k_{obs}=63.33\times10^{-4}s^{-1}$	

Temp. = 40^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.006 moldm^{-3}.

Table 60 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.20 M		0.10 M		0.06 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
5	4.60	0.663	4.56	0.658	4.56	0.658
10	4.24	0.627	4.20	0.623	-	-
15	-	-	-	-	3.84	0.584
20	3.72	0.570	3.72	0.570	3.58	0.554
30	3.20	0.505	3.20	0.505	3.00	0.477
40	2.90	0.462	2.70	0.431	2.46	0.391
50	2.70	0.431	2.40	0.380	2.16	0.334
60	2.30	0.361	2.00	0.301	1.76	0.245
70	2.00	0.301	1.64	0.215	-	-
80	1.80	0.255	1.36	0.133	1.20	0.076
90	-	-	1.06	0.025	-	-
100	1.30	0.114	-	-	-	-
	$^{+1}k_{obs}=2.30\times10^{-4}s^{-1}$		$^{+1}k_{obs}=2.68\times10^{-4}s^{-1}$		$^{+1}k_{obs}=3.07\times10^{-4}s^{-1}$	

Temp. = $30^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.004 $moldm^{-3}$.

Table 61 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.05 M		0.04 M		0.03 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	-	-	-	-	4.60	0.662
5	4.64	0.666	4.34	0.637	4.36	0.639
8	-	-	-	-	4.04	0.606
10	4.30	0.633	4.00	0.602	3.76	0.575
15	3.74	0.572	3.58	0.553	3.40	0.531
20	3.44	0.536	3.20	0.505	2.90	0.462
25	-	-	2.90	0.462	-	-
30	2.84	0.453	2.70	0.431	2.20	0.342
40	2.26	0.354	2.14	0.330	1.76	0.245
50	1.90	0.278	1.70	0.230	1.30	0.114
60	1.50	0.176	1.30	0.114	-	-
65	-	-	1.14	0.056	-	-
70	1.20	0.079	-	-	-	-
	$^{+1}k_{obs}=3.45\times10^{-4}s^{-1}$		$^{+1}k_{obs}=3.84\times10^{-4}s^{-1}$		$^{+1}k_{obs}=4.61\times10^{-4}s^{-1}$	

Temp. = 30°C, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.004 $moldm^{-3}$.

Table-62 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.20 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724
5	4.70	0.670	4.52	0.655
10	4.20	0.623	4.00	0.602
15	3.70	0.568	3.46	0.539
20	3.42	0.534	3.16	0.499
25	3.02	0.480	2.80	0.447
30	2.70	0.431	2.50	0.398
35	2.40	0.380	2.20	0.342
40	2.20	0.342	2.00	0.301
45	-	-	1.72	0.235
50	1.90	0.278	-	-
55	-	-	1.30	0.114
60	1.52	0.182	-	-
70	1.20	0.079	-	-
	$^{+1}k_{obs}=3.45\times10^{-4}s^{-1}$		$^{+1}k_{obs}=4.03\times10^{-4}s^{-1}$	

Temp = $35^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$

$[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [CPC]=0.004 $moldm^{-3}$.

Table-63 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.06 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724
5	4.30	0.633	4.10	0.612
10	3.86	0.586	3.60	0.556
15	3.32	0.521	3.16	0.499
20	2.80	0.447	2.68	0.428
25	2.48	0.394	2.32	0.365
30	2.20	0.342	2.08	0.318
35	1.78	0.250	1.70	0.230
40	1.52	0.182	1.50	0.176
45	1.26	0.100	1.18	0.072
50	1.10	0.041	1.00	0.000
	$^{+1}k_{obs}=4.98\times10^{-4}s^{-1}$		$^{+1}k_{obs}=5.75\times10^{-4}s^{-1}$	

Temp = 35^oC, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2 X 10^{-3} $moldm^{-3}$ $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u = 0.20 $moldm^{-3}$ [CPC]=0.004 $moldm^{-3}$.

Table 64 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.04 M		0.03 M		0.02 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	4.40	0.643	4.20	0.627	3.92	0.599
5	4.00	0.602	4.96	0.597	3.44	0.536
8	-	-	3.42	0.534	2.80	0.447
10	3.30	0.518	3.06	0.485	2.46	0.390
13	-	-	2.76	0.441	2.10	0.322
15	2.80	0.447	2.50	0.398	1.84	2.65
18	-	-	-	-	1.52	0.182
20	2.46	0.390	1.92	0.278	1.36	0.133
23	-	-	-	-	1.12	0.049
25	2.86	0.269	1.60	0.204	1.00	0.000
30	1.50	0.176	1.26	0.100	-	-
35	1.30	0.113	1.06	0.025	-	-
40	1.06	0.025	-	-	-	-
	$^{+1}k_{obs}=6.91\times10^{-4}s^{-1}$		$^{+1}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{+1}k_{obs}=11.51\times10^{-4}s^{-1}$	

Temp. = 35°C, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.004 $moldm^{-3}$.

Table 65 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.07 M		0.06 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
3	4.66	0.668	4.50	0.653	4.48	0.651
5	4.30	0.633	4.20	0.623	4.10	0.612
8	3.70	0.568	3.66	0.563	3.54	0.549
10	3.48	0.541	3.32	0.521	3.24	0.510
13	-	-	-	-	2.80	0.447
15	2.80	0.447	2.50	0.398	2.50	0.398
20	2.20	0.342	2.08	0.318	1.96	0.292
25	1.76	0.245	1.58	0.198	1.52	0.182
30	1.44	0.158	1.32	0.120	1.16	0.064
35	1.24	0.093	1.08	0.033	-	-
	$^{+1}k_{obs}=6.91\times10^{-4}s^{-1}$		$^{+1}k_{obs}=7.67\times10^{-4}s^{-1}$		$^{+1}k_{obs}=8.44\times10^{-4}s^{-1}$	

Temp. = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.004 $moldm^{-3}$.

Table 66 : Effect of the $[H^+]$ on the observed rate constant $(^{+1}k_{obs})$ in the presence of CPC.

$[H^+]$	0.04 M		0.03 M		0.02 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.40	0.643
3	4.40	0.643	4.10	0.612	3.60	0.556
5	4.08	0.610	3.60	0.556	3.00	0.477
8	3.48	0.541	3.00	0.477	2.40	0.380
10	3.08	0.488	2.66	0.425	1.84	0.264
13	2.64	0.421	2.20	0.342	1.50	0.176
15	2.36	0.373	1.90	2.78	1.30	0.114
18	-	-	1.60	0.264	1.00	0.000
20	1.84	0.264	1.38	0.139	-	-
25	1.40	0.146	1.00	0.000	-	-
30	1.00	0.000	-	-	-	-
	$^{+1}k_{obs}=8.83\times10^{-4}s^{-1}$		$^{+1}k_{obs}=11.13\times10^{-4}s^{-1}$		$^{+1}k_{obs}=16.31\times10^{-4}s^{-1}$	

Temp. = $40^{o}C$, [Gly] = 0.03 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.20 $moldm^{-3}$, [CPC]=0.004 $moldm^{-3}$.

OXIDATION OF DL-ALANINE IN THE ABSENCE OF SURFACTANTS

Tables 67 to 69 : Effect of the concentration of DL-alanine on the observed rate constant ($^{01}k_{obs}$).

The concentration of DL-alanine was varied from 0.02 to 0.15 $moldm^{-3}$, at a fixed [CAT] = $2x10^{-3}$ $moldm^{-3}$, $[H^+]$ = 0.05 $moldm^{-3}$, u = 0.15 $moldm^{-3}$ and at a different temperatures (30° to 40°C).

Tables 70 to 72 : Effect of the $[H^+]$ on the observed rate constant ($^{01}k_{obs}$).

The concentration of hydrogen ion is varied from 0.05 to 0.15 $moldm^{-3}$, at a fixed [CAT] = $2x10^{-3}$ $moldm^{-3}$, [Ala] = 0.15 $moldm^{-3}$, u = 0.15 $moldm^{-3}$ and different temperatures (30° to 40°C).

Table 67 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.90	0.690	5.00	0.699	4.80	0.681	4.62	0.665
3	4.60	0.663	4.50	0.653	3.70	0.568	3.18	0.502
5	4.28	0.631	4.12	0.615	3.14	0.497	2.20	0.342
10	3.56	0.551	3.26	0.513	1.82	0.260	1.20	0.079
15	3.04	0.483	2.64	0.422	1.24	0.093	-	-
20	2.60	0.415	2.20	0.342	-	-	-	-
25	2.24	0.350	1.86	0.269	-	-	-	-
30	1.94	0.287	1.58	0.198	-	-	-	-
35	1.70	0.230	1.30	0.114	-	-	-	-
45	1.20	0.079	1.00	0.000	-	-	-	-
50	1.00	0.000	-	-	-	-	-	-
	$^{01}k_{obs}=4.99\times10^{-4}s^{-1}$		$^{01}k_{obs}=7.29\times10^{-4}s^{-1}$		$^{01}k_{obs}=17.27\times10^{-4}s^{-1}$		$^{01}k_{obs}=25.71\times10^{-4}s^{-1}$	

Temp. = 30^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [surfactants]= Nil.

Table 68 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.78	0.679	4.64	0.666	4.64	0.666	4.12	0.615
2	-	-	-	-	-	-	3.06	0.486
3	4.32	0.635	3.98	0.599	3.12	0.494	2.44	0.387
4	-	-	-	-	-	-	1.94	0.288
5	3.90	0.591	3.56	0.551	2.34	0.369	1.66	0.176
6	-	-	-	-	-	-	1.50	0.220
7	-	-	-	-	-	-	1.26	0.100
8	3.40	0.531	2.80	0.447	1.46	0.164	1.16	0.064
10	3.08	0.488	2.54	0.405	1.22	0.086	-	-
13	-	-	2.08	0.318	-	-	-	-
15	2.46	0.391	1.88	0.274	-	-	-	-
18	-	-	1.60	0.204	-	-	-	-
20	2.00	0.301	1.40	0.146	-	-	-	-
25	1.70	0.230	1.20	0.079	-	-	-	-
30	1.42	0.152	-	-	-	-	-	-
35	1.22	0.086	-	-	-	-	-	-
	$^{01}k_{obs}=7.29\times10^{-4}s^{-1}$		$^{01}k_{obs}=11.51\times10^{-4}s^{-1}$		$^{01}k_{obs}=24.56\times10^{-4}s^{-1}$		$^{01}k_{obs}=36.08\times10^{-4}s^{-1}$	

Temp. = 35^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2x10^{-3} moldm^{-3}, $[Na_2S_2O_3]$=5x10^{-3} moldm^{-3}, u=0.15 moldm^{-3}, [surfactants]= Nil.

Table 69 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{01}k_{obs}$) in the absence of surfactants.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.60	0.663	4.62	0.665	4.38	0.641	3.90	0.591
2	4.24	0.627	4.14	0.617	3.38	0.529	2.70	0.431
3	3.96	0.597	3.68	0.566	2.70	0.431	2.00	0.301
4	3.70	0.568	3.34	0.524	2.14	0.330	1.60	0.204
5	3.40	0.531	-	-	1.80	0.255	1.28	0.107
6	-	-	2.74	0.438	1.52	0.182	1.10	0.041
7	-	-	-	-	1.30	0.114	-	-
8	2.80	0.447	2.34	0.369	1.16	0.064	-	-
10	2.46	0.391	2.00	0.301	-	-	-	-
12	-	-	1.76	0.245	-	-	-	-
15	1.86	0.269	1.40	0.146	-	-	-	-
20	1.46	0.164	1.00	0.000	-	-	-	-
25	1.10	0.041	-	-	-	-	-	-
	$^{01}k_{obs}=10.74\times10^{-4}s^{-1}$		$^{01}k_{obs}=16.12\times10^{-4}s^{-1}$		$^{01}k_{obs}=34.54\times10^{-4}s^{-1}$		$^{01}k_{obs}=47.59\times10^{-4}s^{-1}$	

Temp. = 40^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [surfactants]= Nil.

Table 70 : Effect of the $[H^+]$ on the observed rate constant $(^{01}k_{obs})$ in the absence of surfactants.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.90	0.690	4.80	0.681	4.78	0.679	4.62	0.665
3	4.26	0.629	3.90	0.591	3.62	0.558	3.18	0.502
5	3.74	0.573	3.10	0.491	2.76	0.440	2.20	0.342
8	3.00	0.477	2.28	0.358	1.94	0.287	1.60	0.204
10	2.60	0.415	1.96	0.292	1.60	0.204	1.20	0.079
13	2.10	0.322	1.44	0.158	1.14	0.056	-	-
15	1.96	0.292	1.26	0.100	-	-	-	-
18	1.60	0.204	1.00	0.000	-	-	-	-
20	1.40	0.146	-	-	-	-	-	-
25	1.08	0.033	-	-	-	-	-	-
	$^{01}k_{obs}=10.74\times10^{-4}s^{-1}$		$^{01}k_{obs}=16.12\times10^{-4}s^{-1}$		$^{01}k_{obs}=19.19\times10^{-4}s^{-1}$		$^{01}k_{obs}=25.71\times10^{-4}s^{-1}$	

Temp. = 30°C, [Ala] = 0.15 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [surfactants]= Nil.

Table 71 : Effect of the $[H^+]$ on the observed rate constant $(^{01}k_{obs})$ in the absence of surfactants.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.80	0.681	4.62	0.665	4.40	0.643	4.12	0.615
2	4.28	0.631	3.86	0.586	3.62	0.559	3.06	0.486
3	3.82	0.582	3.24	0.510	3.02	0.480	2.44	0.387
4	3.36	0.526	2.72	0.434	2.48	0.394	1.94	0.288
5	3.02	0.480	2.34	0.369	2.04	0.309	1.66	0.176
6	2.56	0.408	1.96	0.292	1.80	0.255	1.50	0.176
7	-	-	-	-	-	-	1.26	0.100
8	2.26	0.354	1.52	0.182	1.36	0.133	1.16	0.064
10	1.92	0.283	1.24	0.093	1.04	0.017	-	-
12	1.56	0.193	1.00	0.000	-	-	-	-
15	1.20	0.079	-	-	-	-	-	-
	$^{01}k_{obs}=17.65\times10^{-4}s^{-1}$		$^{01}k_{obs}=23.79\times10^{-4}s^{-1}$		$^{01}k_{obs}=28.40\times10^{-4}s^{-1}$		$^{01}k_{obs}=36.08\times10^{-4}s^{-1}$	

Temp. = $35^{o}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [surfactants]= Nil.

Table 72 : Effect of the $[H^+]$ on the observed rate constant $(^{01}k_{obs})$ in the absence of surfactants.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.58	0.661	4.38	0.641	4.24	0.627	3.90	0.591
2	3.92	0.593	3.34	0.524	3.12	0.494	2.70	0.431
3	3.34	0.523	2.64	0.422	2.32	0.365	2.00	0.301
4	2.90	0.462	2.22	0.346	1.88	0.274	1.60	0.204
5	2.50	0.398	1.64	0.215	1.48	0.170	1.28	0.107
6	2.20	0.342	1.46	0.164	1.26	0.100	1.10	0.041
7	1.88	0.274	1.34	0.127	1.02	0.008	-	-
8	1.68	0.225	1.08	0.033	-	-	-	-
10	1.36	0.133	-	-	-	-	-	-
	$^{01}k_{obs}=24.56\times10^{-4}s^{-1}$		$^{01}k_{obs}=35.31\times10^{-4}s^{-1}$		$^{01}k_{obs}=39.15\times10^{-4}s^{-1}$		$^{01}k_{obs}=47.59\times10^{-4}s^{-1}$	

Temp. = $40^{o}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [surfactants]= Nil.

OXIDATION OF DL-ALANINE IN THE PRESENCE OF SDS

Tables 73 to 81 : Effect of the concentration of DL-alanine on the observed rate constant (k_{obs}).

The conditions were kept constant as described earlier in the absence of surfactant to see the effect of the concentration of DL-alanine under the condition that [SDS] > cmc (0.01, 0.02 and 0.03 $moldm^{-3}$.

Tables 82 to 84 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$).

The conditions employed were similar as described for the absence of surfactant to see the effect of the $[H^+]$ under the conditions that [SDS] > cmc (0.01 $moldm^{-3}$).

Table 73 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.90	0.690	4.80	0.681	4.80	0.681
3	4.66	0.668	4.50	0.653	4.00	0.602	3.62	0.558
5	4.48	0.651	4.30	0.633	3.32	0.521	2.80	0.447
10	3.96	0.597	3.60	0.556	2.22	0.346	1.64	0.215
15	3.56	0.551	3.04	0.483	1.56	0.193	1.10	0.041
20	3.16	0.499	2.70	0.431	1.20	0.079	-	-
25	-	-	2.30	0.362	-	-	-	-
30	2.62	0.418	2.00	0.301	-	-	-	-
35	-	-	1.86	0.269	-	-	-	-
40	2.14	0.330	-	-	-	-	-	-
45	-	-	1.44	0.158	-	-	-	-
50	1.82	0.260	-	-	-	-	-	-
60	1.50	0.176	1.10	0.041	-	-	-	-
70	1.30	0.113	-	-	-	-	-	-
	$^{-1}k_{obs}=3.45\times10^{-4}s^{-1}$		$^{-1}k_{obs}=5.37\times10^{-4}s^{-1}$		$^{-1}k_{obs}=13.05\times10^{-4}s^{-1}$		$^{-1}k_{obs}=19.19\times10^{-4}s^{-1}$	

Temp. = 30^{O}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.01 moldm^{-3}.

Table 74 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.96	0.695	4.90	0.690	4.80	0.681
3	-	-	4.66	0.668	4.10	0.612	3.76	0.575
5	4.42	0.645	4.24	0.627	3.46	0.539	2.94	0.468
8	-	-	-	-	-	-	2.10	0.322
10	4.12	0.615	3.68	0.566	2.34	0.369	1.80	0.255
13	-	-	-	-	-	-	1.40	0.146
15	-	-	3.14	0.497	1.72	0.235	1.22	0.086
18	-	-	-	-	-	-	1.08	0.033
20	3.50	0.544	2.74	0.438	1.26	0.100	-	-
25	-	-	2.40	0.380	1.00	0.000	-	-
30	3.02	0.480	2.12	0.326	-	-	-	-
35	-	-	1.90	0.278	-	-	-	-
40	2.60	0.415	-	-	-	-	-	-
45	-	-	1.54	0.188	-	-	-	-
50	2.26	0.354	-	-	-	-	-	-
60	2.00	0.301	1.16	0.064	-	-	-	-
70	1.76	0.245	-	-	-	-	-	-
80	1.56	0.193	-	-	-	-	-	-
100	1.28	0.107	-	-	-	-	-	-
	$^{-1}k_{obs}=2.68\times10^{-4}s^{-1}$		$^{-1}k_{obs}=4.61\times10^{-4}s^{-1}$		$^{-1}k_{obs}=11.51\times10^{-4}s^{-1}$		$^{-1}k_{obs}=16.50\times10^{-4}s^{-1}$	

Temp. = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS] = 0.02 moldm^{-3}.

Table 75 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	5.10	0.707	-	-	5.00	0.698
3	-	-	4.70	0.672	4.40	0.643	4.10	0.612
5	4.54	0.657	4.56	0.658	3.90	0.591	3.36	0.526
8	-	-	-	-	-	-	2.36	0.373
10	4.32	0.635	4.00	0.602	2.74	0.437	2.12	0.326
13	-	-	-	-	2.14	0.330	1.66	0.220
15	-	-	3.54	0.549	1.96	0.292	1.44	0.158
18	-	-	-	-	-	-	1.26	0.100
20	3.76	0.575	3.10	0.491	1.54	0.187	1.10	0.041
25	-	-	2.82	0.450	1.26	0.100	-	-
30	3.30	0.518	2.52	0.401	-	-	-	-
35	-	-	2.28	0.357	-	-	-	-
40	2.96	0.471	-	-	-	-	-	-
45	-	-	1.90	0.278	-	-	-	-
50	2.60	0.415	-	-	-	-	-	-
60	2.36	0.373	1.44	0.160	-	-	-	-
70	-	-	-	-	-	-	-	-
75	2.00	0.301	1.10	0.041	-	-	-	-
95	1.60	0.204	-	-	-	-	-	-
125	1.24	0.093	-	-	-	-	-	-
	$^{-1}k_{obs}=2.11\times10^{-4}s^{-1}$		$^{-1}k_{obs}=3.64\times10^{-4}s^{-1}$		$^{-1}k_{obs}=9.59\times10^{-4}s^{-1}$		$^{-1}k_{obs}=13.82\times10^{-4}s^{-1}$	

Temp. = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.03 moldm^{-3}.

Table 76 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.84	0.685	4.86	0.687	4.70	0.672	4.54	0.657
2	-	-	-	-	-	-	3.80	0.579
3	4.52	0.655	4.34	0.637	3.66	0.563	3.20	0.505
4	-	-	-	-	-	-	2.60	0.415
5	4.26	0.629	3.94	0.595	2.88	0.459	2.20	0.342
6	-	-	-	-	-	-	1.96	0.292
8	3.88	0.589	3.58	0.554	2.06	0.314	1.48	0.170
10	3.62	0.558	3.30	0.518	1.76	0.245	1.10	0.041
13	3.30	0.518	2.90	0.462	1.30	0.114	-	-
15	3.12	0.494	2.74	0.438	1.13	0.053	-	-
20	2.62	0.418	2.30	0.361	-	-	-	-
25	-	-	1.90	0.278	-	-	-	-
30	2.00	0.301	-	-	-	-	-	-
35	-	-	-	-	-	-	-	-
40	-	-	1.18	0.071	-	-	-	-
50	1.36	0.133	-	-	-	-	-	-
	$^{-1}k_{obs}=5.37\times10^{-4}s^{-1}$		$^{-1}k_{obs}=8.06\times10^{-4}s^{-1}$		$^{-1}k_{obs}=19.19\times10^{-4}s^{-1}$		$^{-1}k_{obs}=27.63\times10^{-4}s^{-1}$	

Temp. = 35^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.01 moldm^{-3}.

Table 77 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.94	0.694	4.76	0.677	4.66	0.668
2	-	-	-	-	-	-	4.04	0.606
3	-	-	4.52	0.655	3.90	0.591	3.44	0.536
4	-	-	-	-	-	-	2.92	0.465
5	4.50	0.653	4.16	0.619	3.20	0.505	2.56	0.408
6	-	-	-	-	-	-	2.22	0.346
8	-	-	-	-	2.40	0.380	1.72	0.235
10	4.00	0.602	3.60	0.556	2.16	0.334	1.50	0.176
12	-	-	-	-	-	-	1.20	0.079
13	-	-	-	-	1.72	0.235	-	-
15	3.54	0.549	3.00	0.477	1.46	0.164	-	-
18	-	-	-	-	1.18	0.072	-	-
20	3.12	0.494	2.54	0.405	1.10	0.041	-	-
25	-	-	2.20	0.342	-	-	-	-
30	2.48	0.394	-	-	-	-	-	-
35	2.30	0.362	1.70	0.230	-	-	-	-
40	2.00	0.301	-	-	-	-	-	-
45	-	-	1.26	0.100	-	-	-	-
50	1.68	0.225	1.12	0.049	-	-	-	-
60	1.40	0.146	-	-	-	-	-	-
75	1.12	0.049	-	-	-	-	-	-
	$^{-1}k_{obs}=3.83\times10^{-4}s^{-1}$		$^{-1}k_{obs}=6.14\times10^{-4}s^{-1}$		$^{-1}k_{obs}=14.58\times10^{-4}s^{-1}$		$^{-1}k_{obs}=20.73\times10^{-4}s^{-1}$	

Temp. = 35^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2x10^{-3} moldm^{-3}, $[Na_2S_2O_3]$=5x10^{-3} moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.02 moldm^{-3}.

Table 78 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.84	0.685	4.80	0.681	4.66	0.668
2	-	-	-	-	-	-	4.10	0.613
3	-	-	4.60	0.663	4.16	0.619	3.60	0.556
4	-	-	-	-	-	-	3.12	0.494
5	4.64	0.666	4.30	0.630	3.42	0.534	2.40	0.380
6	-	-	-	-	-	-	-	-
8	-	-	-	-	2.68	0.428	1.98	0.297
10	4.10	0.613	3.74	0.573	2.36	0.373	1.66	0.220
13	-	-	-	-	1.96	0.292	-	-
15	3.74	0.573	3.24	0.511	1.70	0.230	1.14	0.057
20	3.36	0.526	2.88	0.459	1.30	0.114	-	-
25	-	-	2.56	0.408	1.00	0.000	-	-
30	2.88	0.459	-	-	-	-	-	-
35	-	-	2.00	0.301	-	-	-	-
40	2.40	0.380	-	-	-	-	-	-
45	-	-	1.60	0.204	-	-	-	-
50	2.00	0.301	-	-	-	-	-	-
60	1.72	0.235	1.30	0.114	-	-	-	-
75	1.40	0.146	-	-	-	-	-	-
90	1.10	0.041	-	-	-	-	-	-
	$^{-1}k_{obs}=3.07\times10^{-4}s^{-1}$		$^{-1}k_{obs}=4.99\times10^{-4}s^{-1}$		$^{-1}k_{obs}=12.66\times10^{-4}s^{-1}$		$^{-1}k_{obs}=19.96\times10^{-4}s^{-1}$	

Temp. = 35^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.03 moldm^{-3}

Table 79 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	5.00	0.698	4.82	0.683	4.54	0.657	3.96	0.597
2	-	-	-	-	3.78	0.577	2.96	0.471
3	4.60	0.663	4.14	0.617	3.12	0.494	2.44	0.387
4	-	-	-	-	2.60	0.415	1.88	0.274
5	4.16	0.619	3.64	0.561	-	-	1.54	0.187
6	-	-	-	-	1.94	0.288	1.36	0.133
7	-	-	-	-	-	-	1.12	0.049
8	3.60	0.556	3.00	0.477	1.46	0.164	1.06	0.025
10	3.32	0.521	2.64	0.422	1.18	0.072	-	-
13	-	-	2.22	0.346	-	-	-	-
15	2.62	0.418	2.00	0.301	-	-	-	-
18	-	-	1.70	0.230	-	-	-	-
20	2.10	0.322	1.54	0.187	-	-	-	-
25	1.74	0.241	1.22	0.086	-	-	-	-
30	1.48	0.170	-	-	-	-	-	-
35	1.10	0.041	-	-	-	-	-	-
	$^{-1}k_{obs}=7.29\times10^{-4}s^{-1}$		$^{-1}k_{obs}=12.28\times10^{-4}s^{-1}$		$^{-1}k_{obs}=26.10\times10^{-4}s^{-1}$		$^{-1}k_{obs}=39.15\times10^{-4}s^{-1}$	

Temp. = 40^{O}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.01 moldm^{-3}.

Table 80 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.90	0.690	4.94	0.694	4.62	0.665	4.52	0.655
2	-	-	-	-	3.92	0.593	3.42	0.534
3	4.56	0.659	4.42	0.645	3.32	0.521	2.88	0.459
4	-	-	-	-	2.84	0.453	2.30	0.362
5	4.28	0.631	3.94	0.595	-	-	1.92	0.283
6	-	-	-	-	2.20	0.342	1.66	0.220
7	-	-	-	-	-	-	1.48	0.170
8	3.84	0.584	3.54	0.549	1.74	0.240	1.24	0.093
10	3.62	0.558	3.24	0.510	1.40	0.146	-	-
12	-	-	-	-	1.18	0.072	-	-
15	3.00	0.477	2.40	0.380	-	-	-	-
20	2.56	0.408	1.96	0.292	-	-	-	-
25	2.20	0.342	1.62	0.209	-	-	-	-
30	-	-	1.34	0.127	-	-	-	-
35	1.60	0.204	1.20	0.079	-	-	-	-
45	1.28	0.107	-	-	-	-	-	-
	$^{-1}k_{obs}=5.75\times10^{-4}s^{-1}$		$^{-1}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{-1}k_{obs}=21.49\times10^{-4}s^{-1}$		$^{-1}k_{obs}=26.86\times10^{-4}s^{-1}$	

Temp. = 40^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2x10^{-3} moldm^{-3}, $[Na_2S_2O_3]$ =5x10^{-3} moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.02 moldm^{-3}

Table 81 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{-1}k_{obs}$) in the presence of SDS.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.84	0.685	4.76	0.677	4.70	0.672
2	-	-	-	-	4.24	0.627	3.80	0.579
3	4.62	0.664	4.38	0.641	3.60	0.556	3.08	0.488
4	-	-	-	-	3.10	0.491	2.54	0.405
5	4.32	0.635	4.00	0.602	-	-	2.16	0.334
6	-	-	-	-	2.52	0.401	1.84	0.265
7	-	-	-	-	-	-	1.60	0.204
8	-	-	-	-	2.02	0.305	1.42	0.152
10	3.70	0.568	3.20	0.505	1.66	0.220	1.10	0.041
12	-	-	-	-	1.40	0.146	-	-
15	3.22	0.508	2.62	0.418	1.10	0.041	-	-
20	2.78	0.444	2.16	0.334	-	-	-	-
25	2.46	0.391	1.82	0.260	-	-	-	-
30	-	-	1.56	0.193	-	-	-	-
35	1.96	0.292	1.34	0.127	-	-	-	-
40	-	-	1.14	0.057	-	-	-	-
45	1.58	0.198	-	-	-	-	-	-
60	1.18	0.072	-	-	-	-	-	-
	$^{-1}k_{obs}=4.99\times10^{-4}s^{-1}$		$^{-1}k_{obs}=6.91\times10^{-4}s^{-1}$		$^{-1}k_{obs}=19.19\times10^{-4}s^{-1}$		$^{-1}k_{obs}=25.33\times10^{-4}s^{-1}$	

Temp. = 40^{o}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.03 moldm^{-3}

Table 82 : Effect of the $[H^+]$ on the observed rate constant $(^{-1}k_{obs})$ in the presence of SDS.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	5.04	0.700	4.82	0.683	4.90	0.690	4.80	0.681
3	4.58	0.661	4.08	0.611	4.04	0.606	3.62	0.558
5	4.10	0.613	3.46	0.539	3.18	0.502	2.80	0.447
8	3.44	0.536	2.64	0.0422	2.44	0.387	1.90	0.278
10	3.08	0.488	2.28	0.357	2.00	0.301	1.64	0.215
13	2.60	0.414	1.80	0.255	1.60	0.204	1.22	0.086
15	2.40	0.380	1.64	0.215	1.36	0.133	1.10	0.041
18	-	-	1.30	0.114	1.10	0.041	-	-
20	1.86	0.269	1.16	0.064	-	-	-	-
25	1.46	0.164	-	-	-	-	-	-
30	1.22	0.086	-	-	-	-	-	-
	$^{-1}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{-1}k_{obs}=12.28\times10^{-4}s^{-1}$		$^{-1}k_{obs}=14.58\times10^{-4}s^{-1}$		$^{-1}k_{obs}=19.19\times10^{-4}s^{-1}$	

Temp. = 30°C, [Ala] = 0.15 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [SDS]= 0.01 moldm^{-3}.

Table 83 : Effect of the $[H^+]$ on the observed rate constant $(^{-1}k_{obs})$ in the presence of SDS.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.78	0.679	4.72	0.674	4.68	0.670	4.54	0.657
2	4.30	0.633	4.16	0.619	4.04	0.606	3.80	0.579
3	4.00	0.602	3.60	0.556	3.42	0.534	3.20	0.505
4	3.66	0.563	3.18	0.502	2.90	0.462	2.60	0.415
5	-	-	-	-	-	-	2.20	0.315
6	3.10	0.491	2.48	0.394	2.24	0.350	1.96	0.292
8	2.68	0.428	2.02	0.305	1.76	0.245	1.48	0.170
10	2.26	0.354	1.66	0.220	1.38	0.139	1.10	0.041
12	1.96	0.292	1.36	0.133	1.12	0.049	-	-
15	1.60	0.204	1.10	0.041	-	-	-	-
20	1.28	0.107	-	-	-	-	-	-
	$^{-1}k_{obs}=13.82\times10^{-4}s^{-1}$		$^{-1}k_{obs}=17.65\times10^{-4}s^{-1}$		$^{-1}k_{obs}=20.72\times10^{-4}s^{-1}$		$^{-1}k_{obs}=27.63\times10^{-4}s^{-1}$	

Temp. = $35^{o}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [SDS]= 0.01 $moldm^{-3}$.

Table 84 : Effect of the $[H^+]$ on the observed rate constant $(^{-1}k_{obs})$ in the presence of SDS.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.40	0.643	4.18	0.621	4.22	0.625	3.96	0.597
2	2.86	0.586	3.42	0.534	3.26	0.513	2.96	0.471
3	3.38	0.529	2.82	0.450	2.68	0.428	2.44	0.387
4	3.00	0.477	2.32	0.365	2.14	0.330	1.88	0.274
5	2.68	0.428	2.04	0.309	1.74	0.240	1.54	0.187
6	2.38	0.376	1.72	0.236	1.56	0.193	1.36	0.133
7	-	-	1.54	0.187	1.30	0.114	1.12	0.049
8	1.94	0.288	1.30	0.114	1.14	0.056	1.06	0.025
9	-	-	1.14	0.057	-	-	-	-
10	1.58	0.198	-	-	-	-	-	-
12	1.32	0.121	-	-	-	-	-	-
15	1.04	0.017	-	-	-	-	-	-
	$^{-1}k_{obs}=21.47\times10^{-4}s^{-1}$		$^{-1}k_{obs}=27.63\times10^{-4}s^{-1}$		$^{-1}k_{obs}=33.01\times10^{-4}s^{-1}$		$^{-1}k_{obs}=39.15\times10^{-4}s^{-1}$	

Temp. = $40^{o}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [SDS]= 0.01 $moldm^{-3}$.

OXIDATION OF DL-ALANINE IN THE PRESENCE OF CPC

Tables 85 to 93 : Eeffect of the concentration of DL-alanine on the observed rate constant ($^{+1}k_{obs}$).

The conditions were kept constant as described earlier in the absence of surfactant to see the effects of the concentration of alanine under the conditions that [CPC] > cmc (0.002, 003, 0.004 moldm^{-3}).

Tables 94 to 96 : Effect of the [H^+] on the observed rate constant ($^{+1}k_{obs}$).

The conditions employed were similar as described for absence of surfactant to see the effects of the [H^+] under the conditions that [CPC] > cmc (0.002 moldm^{-3}).

Table 85 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	-	-	4.64	0.666	4.32	0.635
2	-	-	-	-	3.94	0.595	3.48	0.541
3	4.38	0.641	4.06	0.608	3.34	0.524	2.88	0.459
4	-	-	-	-	2.94	0.468	2.42	0.384
5	3.98	0.599	3.48	0.541	2.50	0.398	1.94	0.288
6	-	-	-	-	2.22	0.346	1.70	0.230
7	-	-	-	-	1.82	0.620	1.48	0.170
8	3.56	0.551	2.84	0.453	1.72	0.235	1.34	0.127
9	-	-	-	-	-	-	1.14	0.071
10	3.26	0.513	2.50	0.398	1.40	0.146	-	-
12	-	-	-	-	1.20	0.079	-	-
13	-	-	2.10	0.322	-	-	-	-
15	2.72	0.434	1.88	0.274	-	-	-	-
18	-	-	1.68	0.225	-	-	-	-
20	2.28	0.357	1.52	0.182	-	-	-	-
23	-	-	1.30	0.114	-	-	-	-
25	1.92	0.283	1.18	0.072	-	-	-	-
30	1.60	0.204	-	-	-	-	-	-
35	1.32	0.120	-	-	-	-	-	-
40	1.20	0.079	-	-	-	-	-	-
	$^{+1}k_{obs}=6.52\times10^{-4}s^{-1}$		$^{+1}k_{obs}=12.28\times10^{-4}s^{-1}$		$^{+1}k_{obs}=22.07\times10^{-4}s^{-1}$		$^{-1}k_{obs}=32.62\times10^{-4}s^{-1}$	

Temp. = $30^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]= 0.002 $mold^{-3}$.

Table 86 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.54	0.657	4.34	0.637	4.28	0.631
2	-	-	4.20	0.623	3.50	0.544	3.26	0.513
3	4.36	0.639	3.70	0.568	2.98	0.474	2.60	0.415
4	-	-	3.36	0.526	2.46	0.391	2.08	0.318
5	4.00	0.602	-	-	2.04	0.309	1.72	0.235
6	-	-	2.66	0.424	1.82	0.260	1.50	0.176
7	-	-	-	-	1.54	0.187	1.28	0.107
8	3.30	0.518	2.36	0.373	1.36	0.133	1.16	0.064
9	-	-	-	-	1.24	0.093	1.02	0.008
10	3.02	0.480	1.92	0.283	1.10	0.041	-	-
13	2.62	0.418	1.52	0.181	-	-	-	-
15	2.40	0.380	1.38	0.139	-	-	-	-
18	2.10	0.322	1.24	0.093	-	-	-	-
20	1.92	0.283	-	-	-	-	-	-
25	1.62	0.209	-	-	-	-	-	-
35	1.22	0.086	-	-	-	-	-	-
	$^{+1}k_{obs}=8.44\times10^{-4}s^{-1}$		$^{+1}k_{obs}=16.31\times10^{-4}s^{-1}$		$^{+1}k_{obs}=28.78\times10^{-4}s^{-1}$		$^{-1}k_{obs}=36.46\times10^{-4}s^{-1}$	

Temp. = 30^{O}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2x10^{-3} moldm^{-3}, $[Na_2S_2O_3]$=5x10^{-3} moldm^{-3}, u=0.15 moldm^{-3}, [CPC]= 0.003 moldm^{-3}.

Table 87 : Effect of the concentration of DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	-	-	4.26	0.629	3.84	0.584
2	-	-	3.90	0.591	2.68	0.428
3	3.80	0.579	3.16	0.447	2.02	0.305
4	-	-	2.82	0.450	1.58	0.198
5	3.24	0.510	-	-	1.26	0.100
6	-	-	2.18	0.338	1.10	0.041
7	-	-	-	-	1.00	0.000
8	2.58	0.411	1.54	0.187	-	-
10	2.00	0.301	1.30	0.114	-	-
13	1.70	0.230	1.00	0.000	-	-
15	1.54	0.187	-	-	-	-
18	1.34	0.127	-	-	-	-
20	1.20	0.079	-	-	-	-
23	1.06	0.025	-	-	-	-
	$^{+1}k_{obs}=13.81\times10^{-4}s^{-1}$		$^{+1}k_{obs}=23.99\times10^{-4}s^{-1}$		$^{+1}k_{obs}=49.89\times10^{-4}s^{-1}$	

Temp. = 30°C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.20 moldm^{-3}, [CPC]=0.004 moldm^{-3}.

Table 88 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.64	0.666	4.54	0.657	4.14	0.617	3.96	0.597
2	-	-	4.04	0.606	3.40	0.531	3.06	0.486
3	4.08	0.611	3.80	0.579	2.80	0.447	2.32	0.365
4	-	-	3.38	0.529	2.38	0.376	1.86	0.269
5	3.60	0.556	-	-	2.08	0.318	1.50	0.176
6	-	-	2.92	0.465	1.60	0.204	1.20	0.079
7	-	-	-	-	1.30	0.114	1.08	0.033
8	2.98	0.474	2.48	0.394	1.10	0.041	-	-
10	2.66	0.424	2.16	0.334	-	-	-	-
13	2.22	0.346	1.80	0.255	-	-	-	-
15	1.94	0.287	1.50	0.176	-	-	-	-
18	1.70	0.230	1.18	0.072	-	-	-	-
20	1.50	0.176	-	-	-	-	-	-
25	1.18	0.072	-	-	-	-	-	-
	$^{+1}k_{obs}=10.36\times10^{-4}s^{-1}$		$^{+1}k_{obs}=14.39\times10^{-4}s^{-1}$		$^{+1}k_{obs}=30.71\times10^{-4}s^{-1}$		$^{-1}k_{obs}=42.22\times10^{-4}s^{-1}$	

Temp. = 35^{o}C, $[H^{+}]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [CPC]= 0.002 moldm^{-3}.

Table 89 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.62	0.665	4.10	0.613	4.04	0.606	3.92	0.593
2	4.10	0.613	3.90	0.591	3.22	0.508	2.90	0.462
3	3.88	0.589	3.40	0.531	2.46	0.390	2.20	0.342
4	3.60	0.556	3.00	0.477	2.00	0.301	1.62	0.209
5	-	-	3.80	0.447	1.60	0.204	1.20	0.079
6	3.10	0.491	2.54	0.405	1.36	0.133	-	-
7	-	-	-	-	1.16	0.04	-	-
8	2.70	0.431	2.10	0.322	1.00	0.000	-	-
10	2.36	0.373	1.76	0.245	-	-	-	-
13	1.94	0.288	1.34	0.127	-	-	-	-
15	1.70	0.230	1.20	0.079	-	-	-	-
20	1.20	0.079	-	-	-	-	-	-
	$^{+1}k_{obs}=13.43\times10^{-4}s^{-1}$		$^{+1}k_{obs}=19.19\times10^{-4}s^{-1}$		$^{+1}k_{obs}=38.38\times10^{-4}s^{-1}$		$^{-1}k_{obs}=49.89\times10^{-4}s^{-1}$	

Temp. = $35^{O}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]= 0.003 $moldm^{-3}$.

Table 90 : Effect of the concentration of DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724
1	4.54	0.657	3.80	0.579	3.50	0.544
2	3.96	0.597	3.06	0.485	2.34	0.369
3	3.60	0.556	2.60	0.415	1.60	0.204
4	3.16	0.499	2.20	0.342	1.26	0.100
5	2.94	0.468	1.84	0.265	1.02	0.008
6	2.50	0.397	1.68	0.225	-	-
7	-	-	1.46	0.164	-	-
8	2.22	0.346	1.30	0.113	-	-
9	-	-	1.12	0.049	-	-
10	1.86	0.269	1.04	0.017	-	-
13	1.36	0.133	-	-	-	-
15	1.10	0.041	-	-	-	-
	$^{+1}k_{obs}=17.27\times10^{-4}s^{-1}$		$^{+1}k_{obs}=32.62\times10^{-4}s^{-1}$		$^{+1}k_{obs}=65.25\times10^{-4}s^{-}$	

Temp. = $35^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]=0.004 $moldm^{-3}$.

Table 91 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.56	0.659	4.30	0.633	4.00	0.602	3.56	0.551
2	4.10	0.613	3.82	0.582	2.86	0.456	2.50	0.398
3	3.84	0.584	3.22	0.507	2.18	0.338	1.86	0.269
4	3.42	0.534	2.92	0.465	1.74	0.240	1.40	0.146
5	-	-	2.68	0.428	1.24	0.093	1.12	0.049
6	2.92	0.465	2.32	0.365	-	-	-	-
8	2.40	0.380	1.98	0.297	-	-	-	-
10	2.00	0.301	1.50	0.176	-	-	-	-
13	1.52	0.182	1.12	0.049	-	-	-	-
15	1.32	0.121	1.00	0.000	-	-	-	-
18	1.10	0.041	-	-	-	-	-	-
	$^{+1}k_{obs}=14.39\times10^{-4}s^{-1}$		$^{+1}k_{obs}=24.95\times10^{-4}s^{-1}$		$^{+1}k_{obs}=44.06\times10^{-4}s^{-1}$		$^{+1}k_{obs}=57.57\times10^{-4}s^{-1}$	

Temp. = $40^{o}C$, $[H^{+}]$ = 0.05 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]= 0.002 $moldm^{-3}$.

Table 92 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.44	0.647	4.20	0.623	3.72	0.570	3.56	0.551
2	4.00	0.602	3.60	0.556	2.62	0.418	2.36	0.373
3	3.50	0.544	3.04	0.483	1.92	2.83	1.66	0.220
4	3.20	0.505	2.62	0.418	1.50	0.187	1.22	0.100
5	2.86	0.456	2.30	0.362	1.12	0.049	1.00	0.000
6	2.60	0.415	1.96	0.292	-	-	-	-
7	-	-	1.72	0.235	-	-	-	-
8	2.16	0.334	1.50	0.176	-	-	-	-
10	1.80	0.255	1.20	0.079	-	-	-	-
12	-	-	1.00	0.000	-	-	-	-
13	1.36	0.133	-	-	-	-	-	-
15	1.18	0.072	-	-	-	-	-	-
	$^{+1}k_{obs}=17.27\times10^{-4}s^{-1}$		$^{+1}k_{obs}=24.95\times10^{-4}s^{-1}$		$^{+1}k_{obs}=49.89\times10^{-4}s^{-1}$		$^{-1}k_{obs}=65.25\times10^{-4}s^{-1}$	

Temp. = 40^{O}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [CPC]= 0.003 moldm^{-3}.

Table 93 : Effect of the concentration of the DL-alanine on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

[Ala]	0.02 M		0.05 M		0.10 M		0.15 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.22	0.625	3.80	0.579	3.32	0.521	3.00	0.477
2	3.60	0.556	3.16	0.499	2.20	0.342	1.90	0.278
3	3.10	0.491	2.50	0.397	1.52	0.182	1.24	0.093
4	2.70	0.431	2.26	0.313	1.10	0.041	-	-
5	2.40	0.380	1.70	0.230	-	-	-	-
6	2.08	0.318	1.40	0.146	-	-	-	-
7	1.86	0.269	1.16	0.064	-	-	-	-
8	1.68	0.225	1.00	0.000	-	-	-	-
10	1.36	0.133	-	-	-	-	-	-
12	1.10	0.041	-	-	-	-	-	-
	$^{+1}k_{obs}=23.99\times10^{-4}s^{-1}$		$^{+1}k_{obs}=38.38\times10^{-4}s^{-1}$		$^{+1}k_{obs}=69.09\times10^{-4}s^{-1}$		$^{+1}k_{obs}=86.36\times10^{-4}s^{-1}$	

Temp. = 40^{O}C, $[H^+]$ = 0.05 moldm^{-3}, [CAT] = 2×10^{-3} moldm^{-3}, $[Na_2S_2O_3]=5\times10^{-3}$ moldm^{-3}, u=0.15 moldm^{-3}, [CPC]= 0.004 moldm^{-3}.

Table 94 : Effect of the $[H^+]$ on the observed rate constant $(^{+1}k_{obs})$ in the presence of CPC.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.58	0.661	4.40	0.643	4.36	0.639	4.32	0.635
2	4.32	0.635	4.02	0.604	3.64	0.561	3.48	0.541
3	3.88	0.589	3.68	0.566	3.08	0.488	2.88	0.459
4	3.48	0.541	3.04	0.483	2.60	0.415	2.42	0.384
5	-	-	2.70	0.432	2.18	0.338	1.94	0.288
6	2.96	0.471	2.32	0.365	1.84	0.265	1.70	0.230
7	-	-	-	-	-	-	1.48	0.170
8	2.46	0.391	1.82	0.260	1.46	0.164	1.34	0.127
9	-	-	-	-	-	-	1.14	0.056
10	2.16	0.334	1.52	0.182	1.10	0.041	-	-
13	1.68	0.235	1.08	0.033	-	-	-	-
15	1.32	0.120	-	-	-	-	-	-
	$^{+1}k_{obs}=16.31\times10^{-4}s^{-1}$		$^{+1}k_{obs}=22.09\times10^{-4}s^{-1}$		$^{+1}k_{obs}=25.91\times10^{-4}s^{-1}$		$^{+1}k_{obs}=32.62\times10^{-4}s^{-1}$	

Temp. = $30^{o}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]=0.002 $moldm^{-3}$.

Table 95 : Effect of the $[H^+]$ on the observed rate constant ($^{+1}k_{obs}$) in the presence of CPC.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.36	0.639	4.30	0.633	4.06	0.608	3.96	0.597
2	2.86	0.586	3.54	0.549	3.30	0.518	3.06	0.486
3	3.30	0.518	3.04	0.488	2.74	0.431	2.32	0.365
4	2.92	0.465	2.50	0.398	2.06	0.314	1.86	0.269
5	2.76	0.441	2.10	0.322	1.62	0.209	1.50	0.176
6	2.36	0.373	1.80	0.255	1.36	0.133	1.20	0.079
7	-	-	-	-	1.20	0.079	1.08	0.033
8	1.90	0.278	1.38	0.139	1.02	0.008	-	-
9	-	-	1.10	0.041	-	-	-	-
10	1.54	0.187	-	-	-	-	-	-
12	1.18	0.071	-	-	-	-	-	-
	$^{+1}k_{obs}=21.11\times10^{-4}s^{-1}$		$^{+1}k_{obs}=26.86\times10^{-4}s^{-1}$		$^{+1}k_{obs}=34.54\times10^{-4}s^{-1}$		$^{+1}k_{obs}=42.22\times10^{-4}s^{-1}$	

Temp. = $35^{o}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]=0.002 $moldm^{-3}$.

Table 96 : Effect of the $[H^+]$ on the observed rate constant $(^{+1}k_{obs})$ in the presence of CPC.

$[H^+]$	0.15 M		0.10 M		0.075 M		0.05 M	
Time (min)	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R	Titrant R (ml)	log R
0	5.30	0.724	5.30	0.724	5.30	0.724	5.30	0.724
1	4.10	0.612	4.00	0.602	3.80	0.579	3.56	0.551
2	3.50	0.554	3.10	0.491	2.90	0.462	2.50	0.398
3	2.92	0.465	2.46	0.391	2.08	0.318	1.86	0.269
4	2.40	0.380	1.90	0.279	1.50	0.176	1.40	0.146
5	2.08	0.318	1.60	0.206	1.28	0.107	1.12	0.049
6	1.80	0.255	1.36	0.133	1.02	0.008	-	-
7	1.54	0.187	1.10	0.041	-	-	-	-
8	1.28	0.107	-	-	-	-	-	-
	$^{+1}k_{obs}=28.78\times10^{-4}s^{-1}$		$^{+1}k_{obs}=38.38\times10^{-4}s^{-1}$		$^{+1}k_{obs}=46.06\times10^{-4}s^{-1}$		$^{+1}k_{obs}=57.57\times10^{-4}s^{-1}$	

Temp. = $40^{O}C$, [Ala] = 0.15 $moldm^{-3}$, [CAT] = 2×10^{-3} $moldm^{-3}$, $[Na_2S_2O_3]=5\times10^{-3}$ $moldm^{-3}$, u=0.15 $moldm^{-3}$, [CPC]=0.002 $moldm^{-3}$.

RESULTS AND DISCUSSION

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The oxidative decarboxylation of amino acids has attracted interest of several research groups. A number of inorganic and organic oxidants have been used to investigate the kinetics of these reactions. However, the role of micelles in the oxidative decarboxylation of biomolecules has been studied in very limited cases whereas, the micelles catalyzed hydrolysis of a large number of substrates have been fully investigated. The investigation was carried out in order to make a comparative study of the impact of anionic and cationic surfactants on the kinetic parameters and mechanism of decarboxylation of glycine and alanine.

The kinetics of oxidative decarboxylation of amino acids by acid permangnate was studied by **Hussain and Ahmad**[1-6] both in the absence and presence of sodium dodecyl sulfate (SDS). However, chloramine-T which can be used under physiological condition to bring about decarboxylation of amino acids has been not fully investigated in the presence of anioic and cationnic surfactants. The active oxidizing species in chloramine-T system may involves a cationnic species (Cl^+) and /or neutral species (HOCl) and /or anionic species such as (RNCl). In view of such diverse mode of action the effect of anionic and cationic micelles may be significant in modifying reaction kinetics.

GENERAL FEATURES OF KINETIC OF DECARBOXYLATION OF GLYCINE AND ALANINE :

It is observed that the decarboxylation of glycine and alanine in the absence of surfactant as well as in the presence of anionic micelle of sodium dodecyl sulfate (SDS) and cationic micelle of cetyl pyridinium chloride (CPC) follow a pseudo first order kinetics. From the plots of log R versus time, (where R is the titration value at time , t) these pseudo first order constants in the absence of any surfactant, $^{01}k_{obs}$, have been obtained under different experimental conditions. The slopes of the plots of $^{01}k_{obs}$ versus [amino acid] at different concentrations of surfactant, hydrogen ion and temperatures, give the second order rate constant as ^{02}k ^{-2}k and ^{+2}k (Table 1 and 2) signifying reactions in the absence of surfactant and in the presence of SDS and CPC respectively. The observed rate law may be written as :

$$-\frac{d\,[CAT]}{dt} = {}^{2i}k\,[\text{amino acid}]\,[CAT] \text{-------(1)}$$

Where ^{2i}k in the absence of any surfactant is represented as ^{02}k and in the presence of SDS as ^{-2}k and in the presence of CPC as ^{+2}k.

The preliminary investigations showed that the ionic strength of the medium had no effect on the observed rate constant. In view of the above, effect of variation of hydrogen ion concentration on the reaction was

TABLE-1 : TEMPERATURE DEPENDENCE OF $^{2}k_{G}$ FOR GLYCINE

Temps. (°C)	In the absence of surfactants	[SDS]=0.01 M	[SDS]=0.02 M	[SDS]=0.03 M	[CPC]=0.002 M	[CPC]=0.004 M	[CPC]=0.006 M
	$^{02}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-2}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-2}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-2}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+2}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+2}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+2}k_{G} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)
30	82.5	62.5	55.0	47.5	90.0	125.0	212.0
35	130.0	100.0	80.0	70.0	142.5	202.5	350.0
40	210.0	150.0	125.0	110.0	225.0	287.0	550.0

$[H^{+}]$ = 0.05 mol dm^{-3} and [CAT] = 2 x 10^{-3} mol dm^{-3}

TABLE-2 : TEMPERATURE DEPENDENCE OF $^{2}k_{A}$ FOR ALANINE

Temps. (°C)	In the absence of surfactants	[SDS]=0.01 M	[SDS]=0.02 M	[SDS]=0.03 M	[CPC]=0.002 M	[CPC]=0.003 M	[CPC]=0.004 M
	$^{0}{}^{2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+2}k_{A} \times 10^{4}$ ($s^{-1}mol^{-1}dm^{3}$)
30	170.0	132.0	104.0	92.0	190.0	230.0	264.0
35	240.0	190.0	144.0	126.0	270.5	312.5	360.0
40	324.0	240.0	190.0	170.0	360.0	400.0	480.0

$[H^{+}]$ = 0.05 mol dm^{-3} and [CAT] = 2×10^{-3} mol dm^{-3}

observed by changing the concentration of HCl. It was observed that the reaction slows down with increase in the hydrogen ion concentration both in the absence and presence of any surfactant. In all these cases a plot of second order rate constant ^{2}k versus $1/[H^{+}]$ was found to be linear (vide Figs. 2 a,b,c and 4 a,b,c). These plots gave a positive intercept, indicating the reaction consisted of two simultaneous routes of which one remains unaffected by hydrogen ion concentration, represented by the intercept of these plots, giving the second ordre rate constant $^{02}k_{H}$, $^{-2}k_{H}$ and $^{+2}k_{H}$ in the absence of any surfactant, in the presence of SDS and in the presence of CPC respectively. On the other hand the slopes of these plots represtented a reaction path adversely affected by the hydrogen ion concentration. From these slopes the first order rate constants $^{01}k_{H}$, $^{-1}k_{H}$ and $^{+1}k_{H}$ (Table 3 and 4) were determined in the absence of any surfactant, in the presence of SDS and in the presence of CPC respectively. The equation (1) may, therefore, be written as ,

$$-\frac{d\,[CAT]}{dt} = \{\, {}^{2i}k + {}^{1i}k / [H^{+}] \,\}\, [\text{amino acid}]\, [CAT] \qquad \text{----} \quad (2)$$

The above equation may be obtained from the mechanism proposed and all major kinetics features may be also justified.

TABLE-3 : TEMPERATURE DEPENDENCE OF $^{1}k_{HG}$ AND $^{2}k_{HG}$ *

Temps. (°C)	In the absence of surfactants		In the presence of SDS •		In the presence of CPC ▲	
	$^{1}k_{HG} \times 10^{3}$ (s^{-1})	$^{2}k_{HG} \times 10^{3}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{1}k_{HG} \times 10^{3}$ (s^{-1})	$^{2}k_{HG} \times 10^{3}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{1}k_{HG} \times 10^{3}$ (s^{-1})	$^{2}k_{HG} \times 10^{3}$ ($s^{-1}mol^{-1}dm^{3}$)
30	0.28	4.0	0.25	1.0	0.28	6.0
35	0.42	7.2	0.32	2.5	0.60	7.5
40	0.54	13.2	0.40	8.8	0.90	10.0

* $^{1}k_{HG}$ and $^{2}k_{HG}$ are obtained from slopes and intercepts of $^{2}k_{G}$ versus $1/[H^{+}]$.

• [SDS] = 0.01 mol dm^{-3}, ▲ [CPC] = 0.004 mol dm^{-3}, [Gly] = 0.03 mol dm^{-3} and [CAT] = 2×10^{-3} mol dm^{-3}

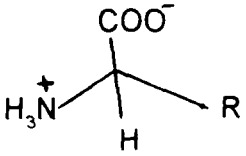
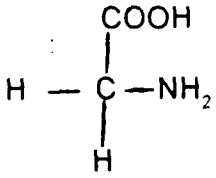
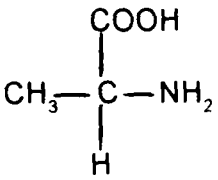
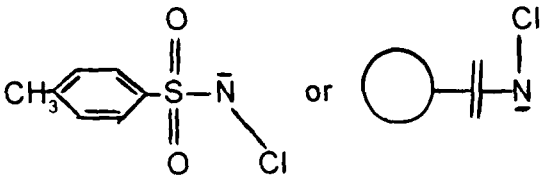
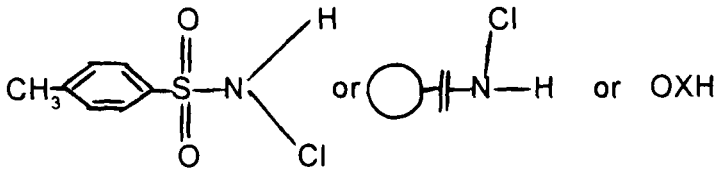
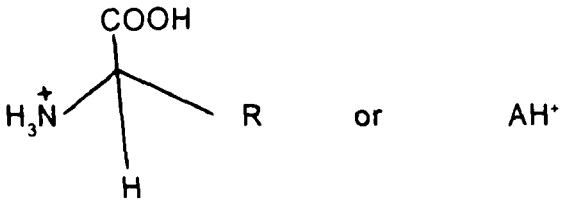
TABLE-4 : TEMPERATURE DEPENDENCE OF $^{1}k_{HA}$ AND $^{2}k_{HA}$ *

Temps. (°C)	In the absence of surfactants		In the presence of SDS o		In the presence of CPC Δ	
	$^{01}k_{HA} \times 10^{3}$ (s^{-1})	$^{02}k_{HA} \times 10^{3}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{-1}k_{HA} \times 10^{3}$ (s^{-1})	$^{-2}k_{HA} \times 10^{3}$ ($s^{-1}mol^{-1}dm^{3}$)	$^{+1}k_{HA} \times 10^{3}$ (s^{-1})	$^{+2}k_{HA} \times 10^{3}$ ($s^{-1}mol^{-1}dm^{3}$)
30	0.72	3.0	0.48	3.2	0.80	6.4
35	0.84	6.9	0.60	5.4	1.04	8.0
40	1.10	12.0	1.00	8.5	1.40	11.0

* $^{1}k_{HA}$ and $^{2}k_{HA}$ are obtained from slopes and intercepts of $^{2}k_{A}$ versus $1/[H^{+}]$.

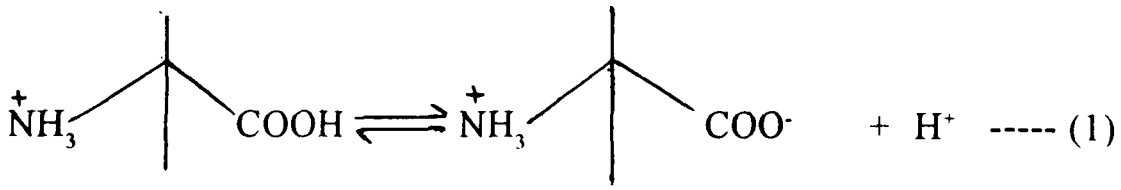
o [SDS] = 0.01 mol dm^{-3}, Δ [CPC] = 0.002 mol dm^{-3}, [Ala] = 0.15 mol dm^{-3} and [CAT] = 2×10^{-3} mol dm^{-3}

THE SYMBOLS USED IN THE DISCUSSION ARE

Symbols	What it represents
 or [A]	Amino acid
 or [Gly]	Glycine
 or [Ala]	Alanine
 or OX	Chloramine-T
 or OXH	Protonated Chloramine-T
$[A]_0$	Initial concentration of amino acid
$[OX]_T$	Total concentration of oxidant at time, t
 or AH^+	Protonated amino acid
S^{n-}	Negatively charged micelle for SDS
S^{m+}	Positively charged micelle for CPC
D_0	Concentration of surfactant

REACTION MECHANISM IN THE ABSENCE OF SURFACTANTS

The oxidative decarboxylation of amino acids has raised several interesting questions. Some authors have suggested that amino group is the most likely reactiavae site[7-12] but other have favoured attack at the carboxylic group[13-16]. In certain cases protonated amino group has been proposed as the active site. It is reasonable to assume that the oxidant attack requiring withdrawal of electron from the protonated amino acid is less likely to occur. However, in strong acidic medium amino acid is completely protonated.



$$\underset{(AH^+)}{R\text{-}CH(NH_3^+)\text{-}COOH} \rightleftharpoons \underset{(A)}{R\text{-}CH(NH_3^+)\text{-}COO^-} + H^+ \quad \text{----- (1)}$$

Under these conditions the oxidant attack at the carboxylic group may be favoured. The oxidant, sodium N-chloro-p-toluenesulphonamide may also produce a large number of oxidizing species such as, HOCl, Cl_2, and H_2OCl^+. However, it has been shown that at low pH, the principal species present in the acidic medium are RNHCl and RNCl involved in the equilibrium.

$$\underset{(OXH)}{RNHCl} \rightleftharpoons \underset{(O\bar{X})}{R\bar{N}Cl} + H^+ \quad \text{---------- (2)}$$

In view of the above, following mechanism for oxidative decarboxylation of glycine and alanine may be proposed in the absence of any surfactant.

$$AH^+ \overset{K_A}{\rightleftharpoons} A + H^- \qquad \text{----------} \qquad (1)$$

$$OXH \overset{K_O}{\rightleftharpoons} \bar{O}\bar{X} + H^- \qquad \text{----------} \qquad (2)$$

$$A + OXH \xrightarrow{k_1} \text{-------} \qquad \text{----------} \qquad (3)$$

$$A + \bar{O}\bar{X} \xrightarrow{k_2} \text{-------} \qquad \text{----------} \qquad (4)$$

$$AH^+ + OXH \xrightarrow{k_3} \text{-------} \qquad \text{----------} \qquad (5)$$

K_A and K_O may be defined as

$$K_A = \frac{[A]\,[H^+]}{[AH^+]} \text{ and } K_O = \frac{[\bar{O}\bar{X}]\,[H^+]}{[OXH]}$$

Using the mass-balanced equation for the amino acid concentration, [A] and $[AH^+]$ may be expressed in terms of $[A]_0$ as below :

$$[A]_0 = [A] + [AH^+]$$

$$= [A] + \frac{[A]\,[H^+]}{K_A}$$

$$[A]_0 = \frac{[A]}{K_A}(K_A + [H^+]) \text{---------- (6)}$$

Also for $[AH^+]$, we get

$$[A]_0 = [A] + [AH^+]$$

$$= \frac{K_A [AH^+]}{[H^+]} + [AH^-]$$

$$= [AH^-] (K_A / [H^+] + 1)$$

$$= \frac{[AH^-]}{[H^-]} (K_A + [H^+]) \quad \text{----------} \quad (7)$$

Similarly using the mass-balanced equation for the oxidant concentration, $[OX]$ and $[OXH]$ may be obtained in terms of $[OX]_T$ as ;

$$[OX]_T = [O\bar{X}] + [OXH]$$

$$= [O\bar{X}] + \frac{[O\bar{X}] [H^+]}{K_O}$$

$$= \frac{[O\bar{X}]}{K_O} (K_O + [H^-]) \quad \text{----------} \quad (8)$$

Also $$= \frac{K_O [OXH]}{[H^+]} + [OXH]$$

$$= [OXH] (K_O / [H^+] + 1)$$

$$= \frac{[OXH]}{[H^+]} (K_O + [H^+]) \quad \text{----------} \quad (9)$$

reaction rate $= (k_1 [OXH]+k_2[\overline{OX}]) [A]+(k_3[OXH]+k_4[\overline{OX}])[AH^-]$

---------- (10)

simplifying the product,

$$(K_A + [H^+])\ (K_O + [H^+]) = K_AK_O+(K_A + K_O)\ [H^+] + [H^+]^2$$

$$\approx (K_A + K_O)\ [H^+]$$

assuming that $[H^-]^2$ term is negligible and $K_A\ K_O << 1$

$$\text{reaction rate} = (k_1 [H^-] + k_2 K_O)\ \frac{K_A [A]_0 [OX]_T}{(K_A + K_O) [H^-]}$$

$$+ (k_3 [H^+] + k_4K_A\ )\ \frac{[A]_0 [H^-] [OX]_T}{(K_A + K_O) [H^+]}$$

$$= (k_1K_A + k_2K_A K_O / \ [H^-] + k_3 [H^+] + k_4K_O) \frac{[A]_0 [OX]_T}{(K_A + K_O)}$$

assuming $k_3 << 1$

$$\text{reaction rate} = \{ \frac{k_1K_A + k_4 K_O}{(K_A + K_O)} + \frac{k_2K_A K_O}{(K_A + K_O)} . \frac{1}{[H^+]} \}[A]_0 [OX]_T$$

----------(11)

$$= {}^{01}k_{obs} [OX]_T$$

$$= {}^{02}k\ [A]_0 [OX]_T$$

where

$${}^{01}k_{obs} = \{ \frac{k_1K_A + k_4 K_O}{(K_A + K_O)} + \frac{k_2K_A K_O}{(K_A + K_O)} . \frac{1}{[H^+]} \}$$ -------- (12)

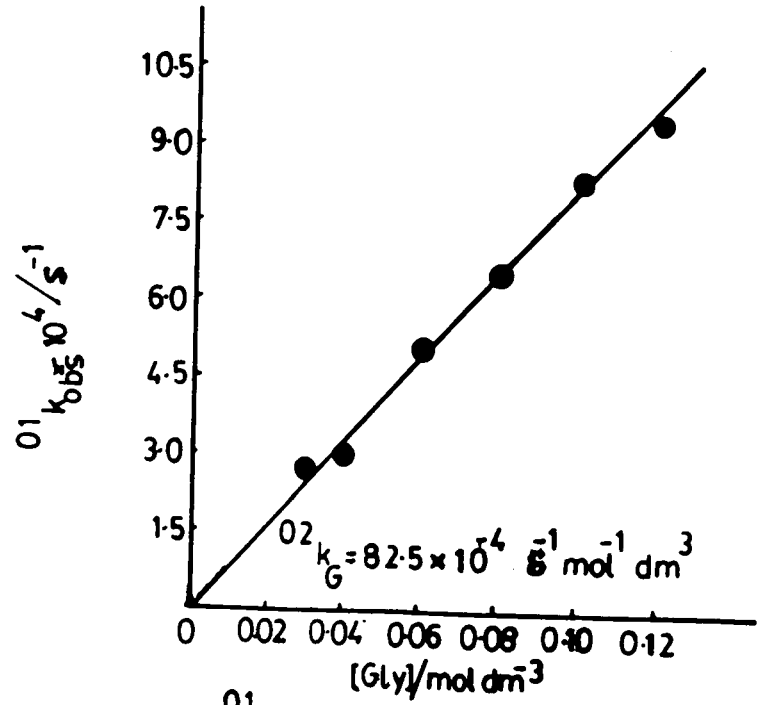


Figure 1a : Plot of $^{01}k_{obs}$ VS [Gly] in the absence of surfactants

Temp. = 30°C , $[H^+]$ = 0·05 mol dm^{-3}, [CAT] = 2 × 10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [Surfactants] = Nil .

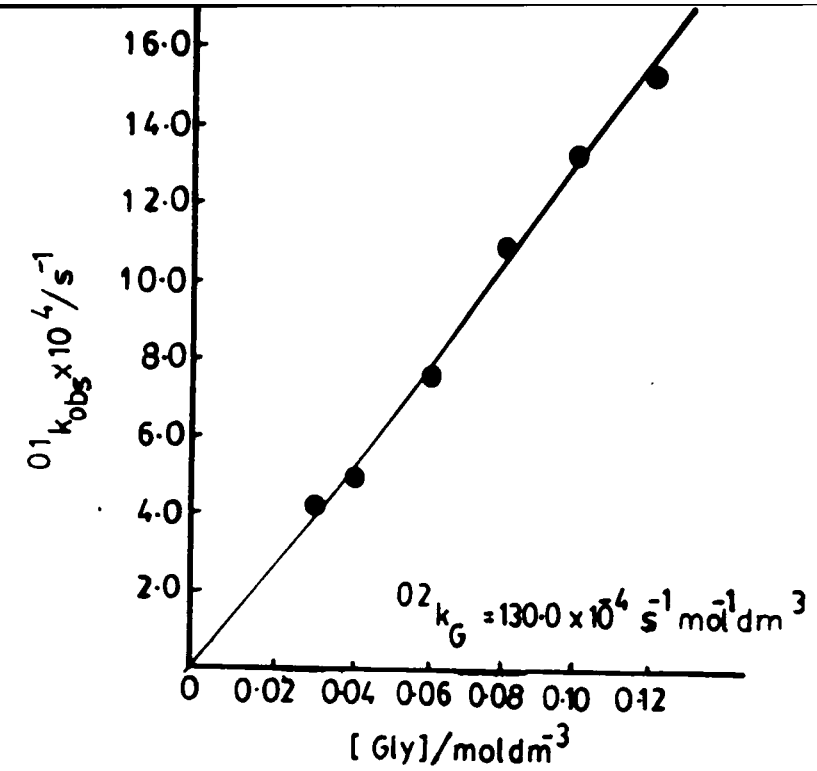


Figure 1 b : Plot of $^{01}k_{obs}$ VS [Gly] in the absence of surfactants

Temp. = 35°C, $[H^+]$ = 005 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [Surfactants] = Nil.

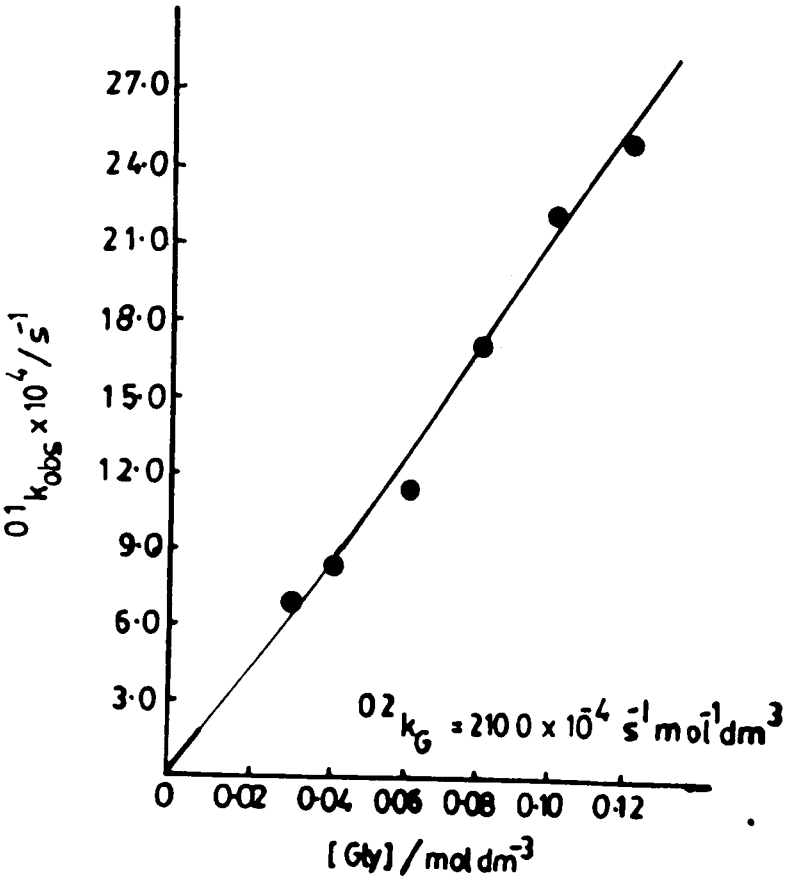


Figure 1c : Plot of $^{01}k_{obs}$ VS [Gly] in the absence of surfactants

Temp = 40°C, $[H^+]$ = 005 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [Surfactants] = Nil.

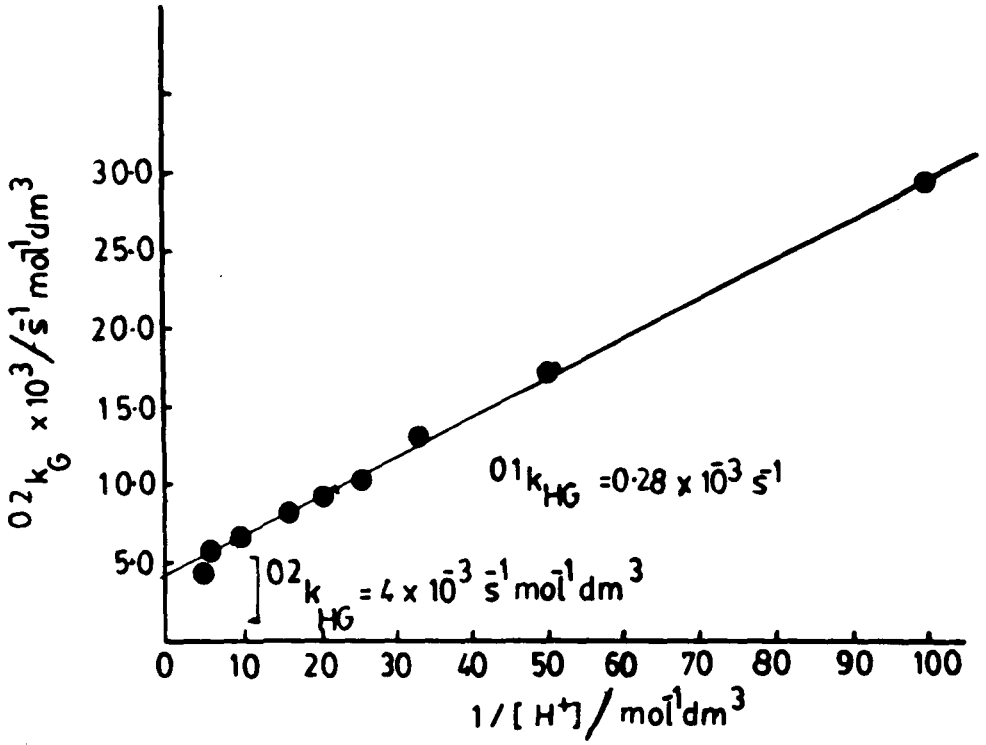


Figure 2a : Plot of $^{02}k_G$ VS $1/[H^+]$ in the absence of surfactants

Temp = 30°C, [Gly] =0·03 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [Surfactants] = Nil.

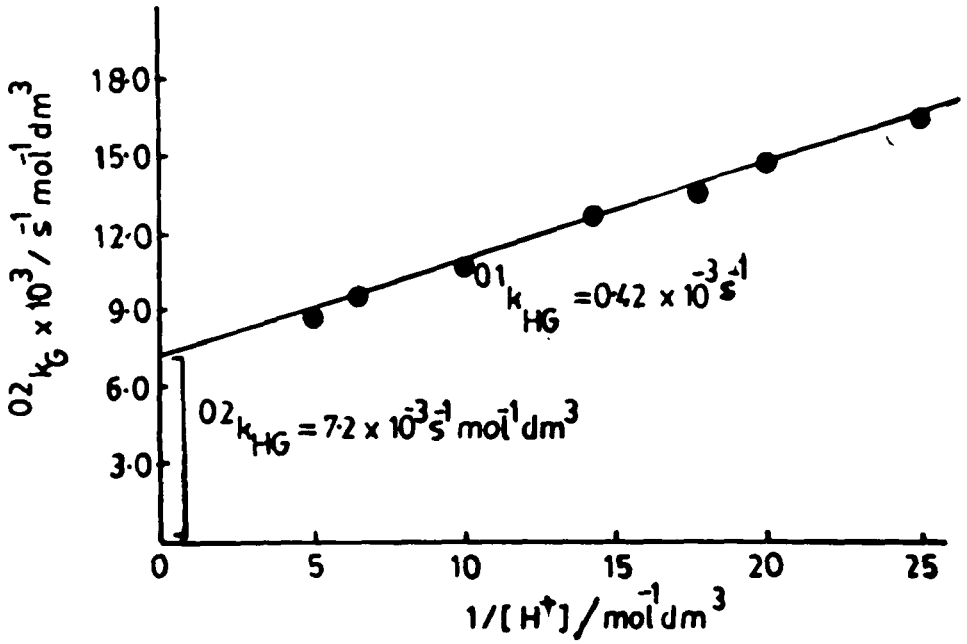


Figure 2b : Plot of $^{02}k_G$ VS $1/[H^+]$ in the absence of surfactants

Temp = 35°C, [Gly] =0·03 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [Surfactants] = Nil.

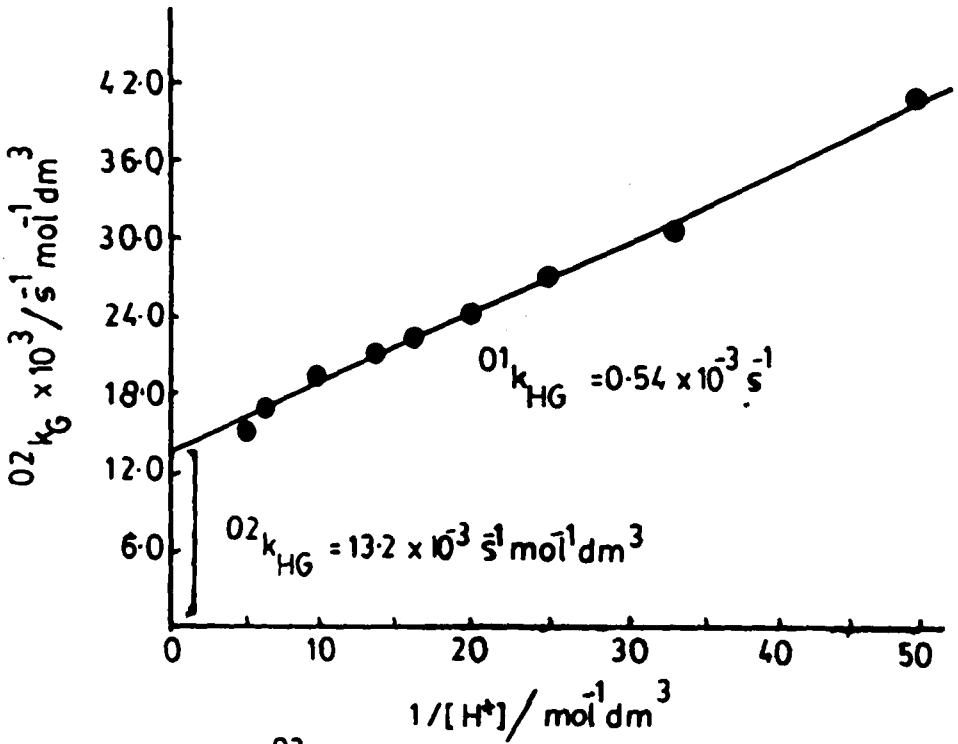


Figure 2c: Plot of $^{02}k_G$ VS $1/[H^+]$ in the absence of surfactants

Temp. = 40°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [Surfactants] = Nil.

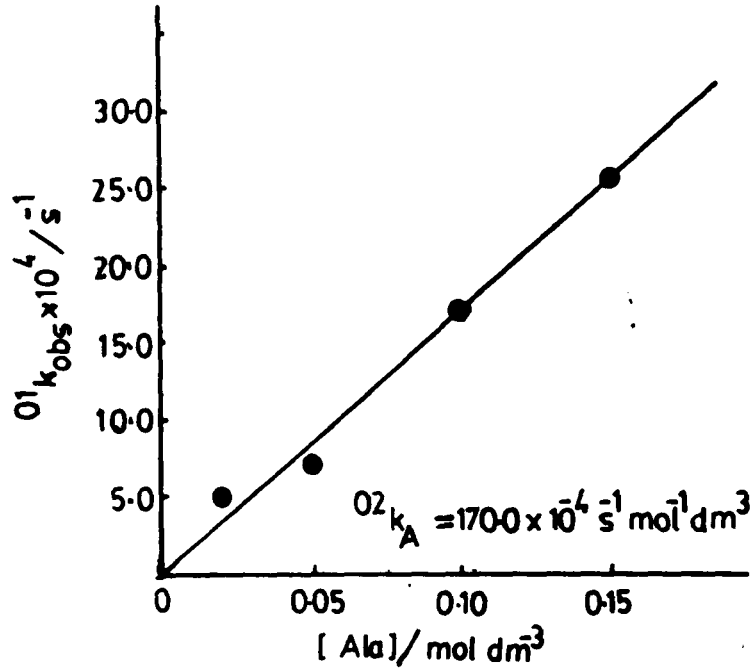


Figure 3a: Plot of $^{01}k_{obs}$ VS [Ala] in the absence of surfactants

Temp = 30°C, $[H^+] = 0{\cdot}05$ mol dm^{-3}, $[CAT] = 2 \times 10^{-3}$ mol dm^{-3},

$\mu = 0{\cdot}15$ mol dm^{-3}, [Surfactants] = Nil.

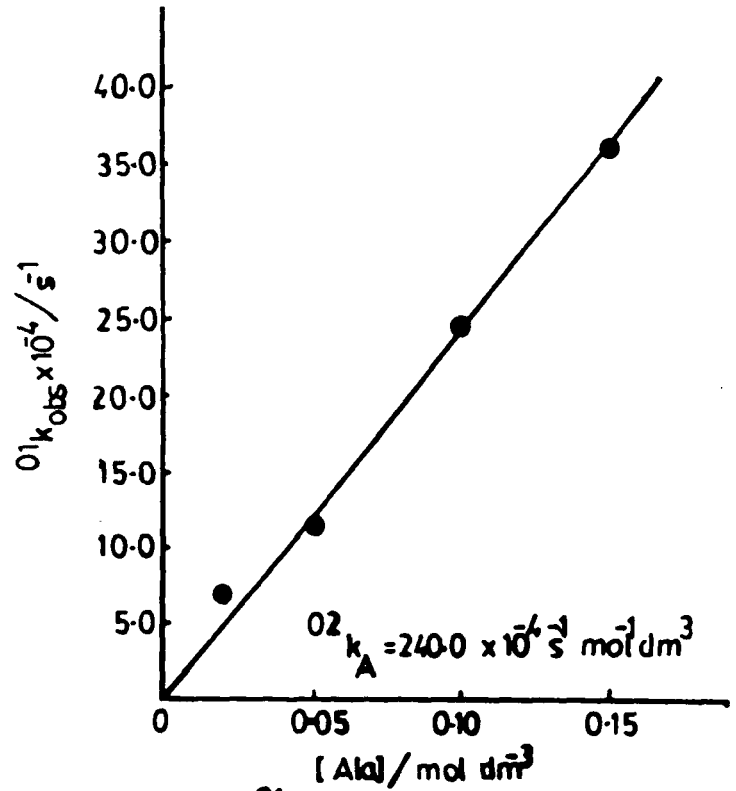


Figure 3b Plot of $^{01}k_{obs}$ VS [Ala] in the absence of surfactants

Temp. = 35°C, $[H^+] = 0{\cdot}05$ mol dm^{-3}, $[CAT] = 2 \times 10^{-3}$ mol dm^{-3},

$\mu = 0{\cdot}15$ mol dm^{-3}, [Surfactants] = Nil.

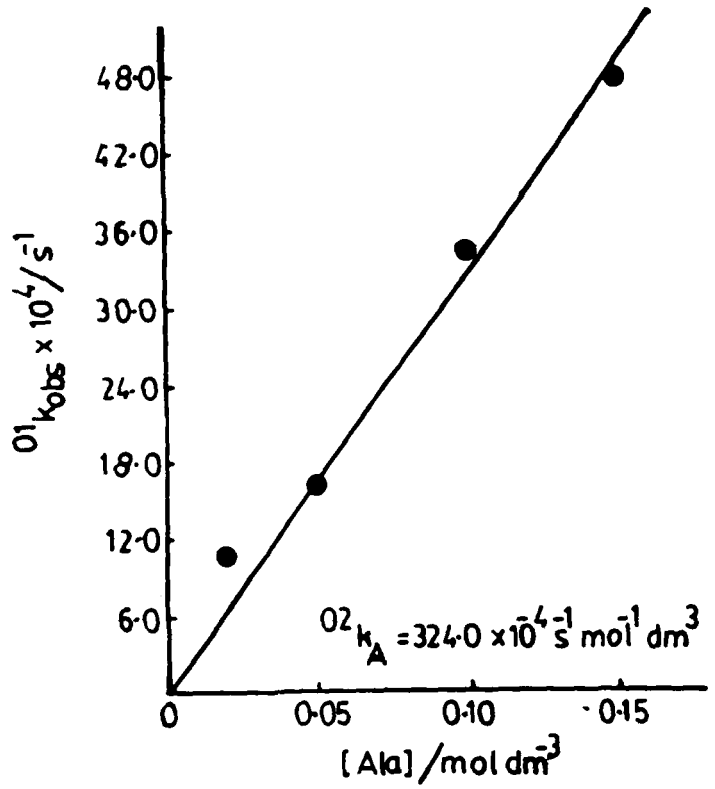


Figure 3c: Plot of $^{01}k_{obs}$ VS [Ala] in the absence of surfactants Temp. = 40°C, $[H^+]$ = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3}, μ = 0·15 mol dm^{-3}, [Surfactants] = Nil.

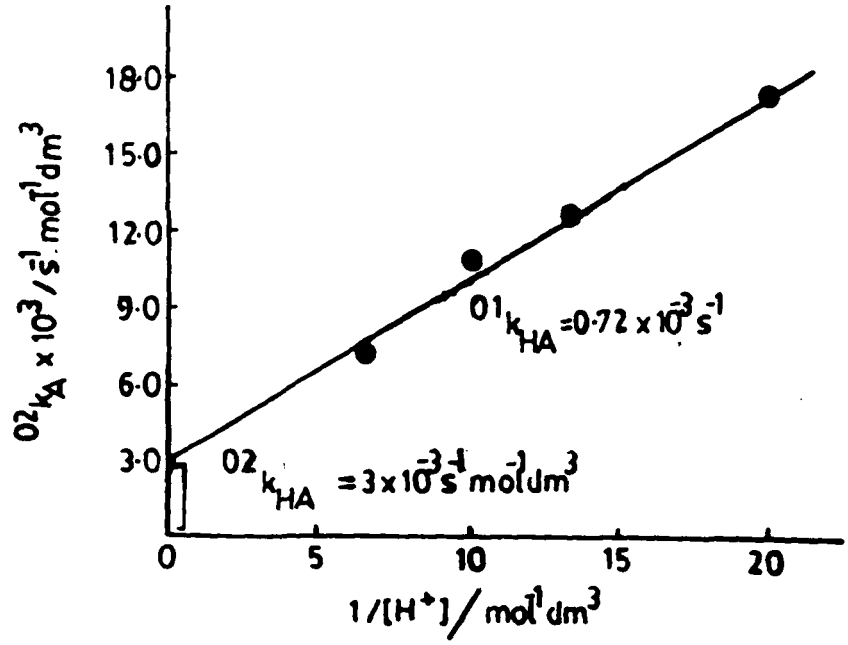


Figure 4a: Plot of $^{02}k_A$ VS $1/[H^+]$ in the absence of surfactants Temp. = 30°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3}, μ = 0·15 mol dm, [Surfactants] = Nil

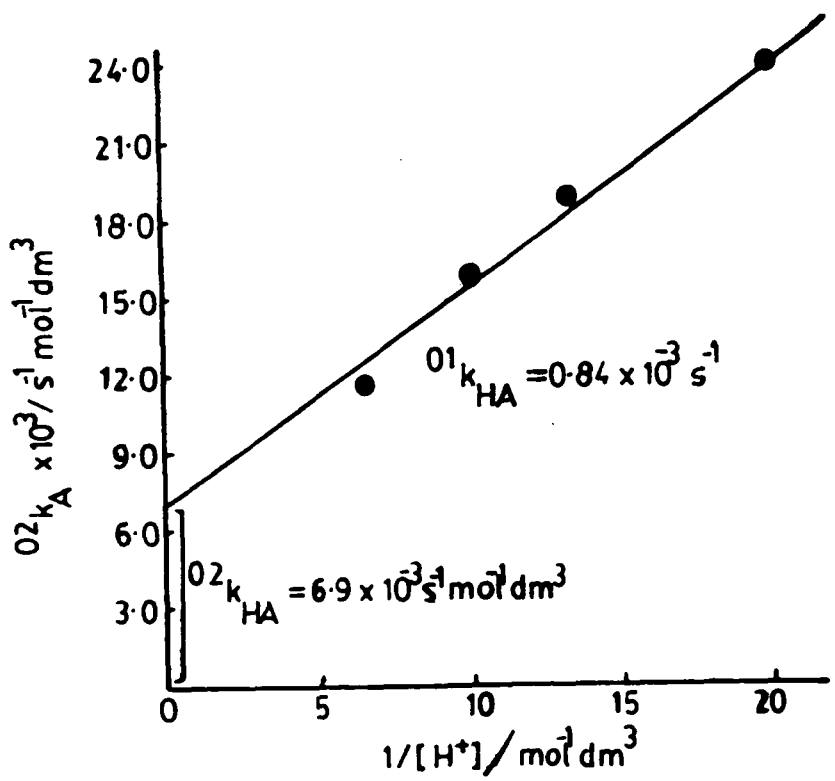


Figure 4b: Plot of $^{02}k_A$ VS $1/[H^+]$ in the absence of surfactants

Temp = 35°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [Surfactants] = Nil

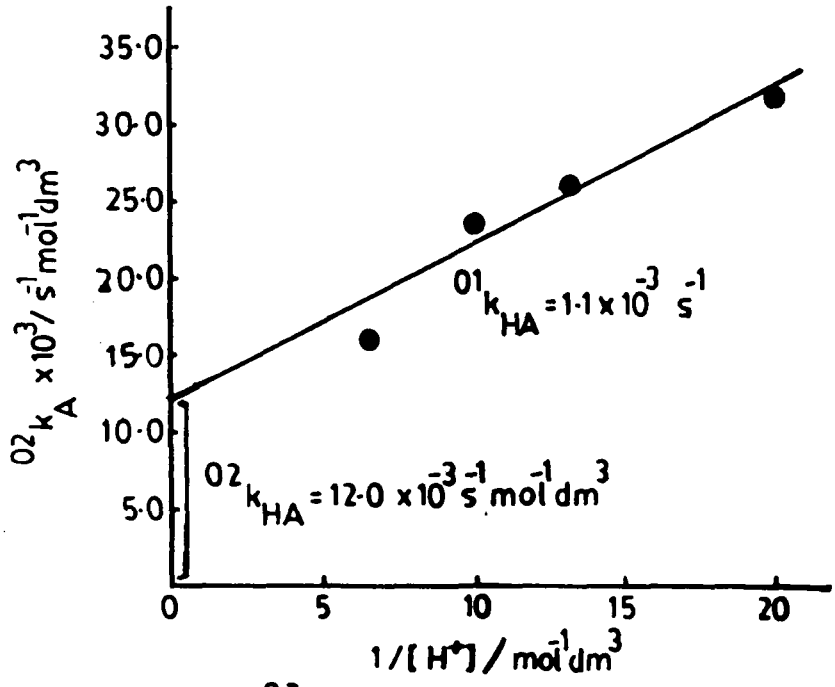


Figure 4c Plot of $^{02}k_A$ VS $1/[H^+]$ in the absence of surfactants

Temp. = 40°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm, [Surfactants] = Nil

or

$$^{02}k = \frac{^{01}k_{obs}}{[A]_0} = \left\{ \frac{k_1K_A + k_4K_O}{(K_A + K_O)} + \frac{k_2K_A K_O}{(K_A + K_O)} \cdot \frac{1}{[H^+]} \right\} \text{ ------- (13)}$$

$$= \left\{ ^{02}k_H + ^{01}k_H \cdot \frac{1}{[H^+]} \right\} \text{ ------- (14)}$$

where

$$^{02}k_H = \frac{k_1K_A + k_4K_O}{(K_A + K_O)}$$

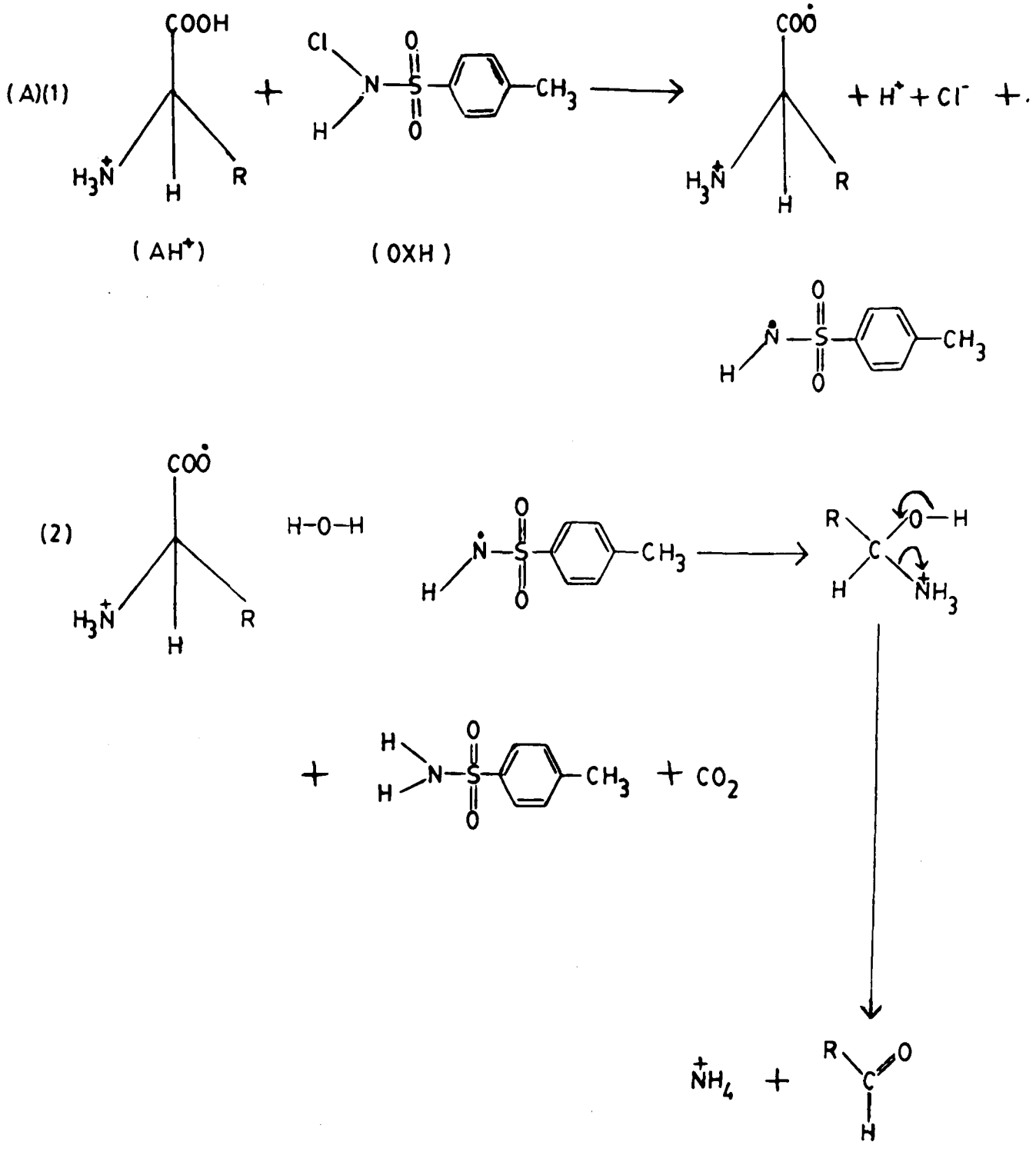
and

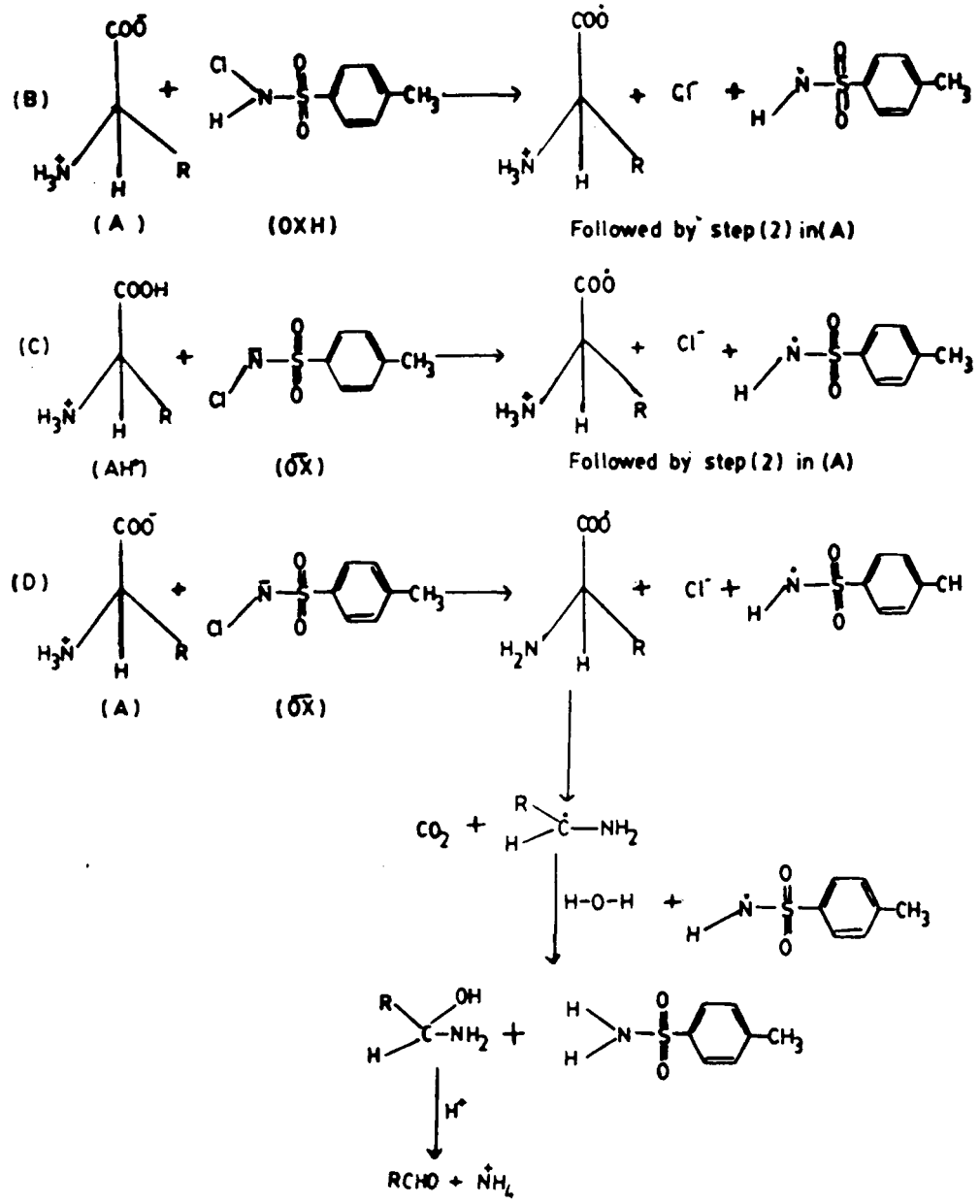
$$^{01}k_H = \frac{k_2K_A K_O}{(K_A + K_O)}$$

The first order observed rate constants, $^{01}k_{obs}$, have been obtained from the plots of log R versus time where R is the titration value at time, t,under different conditions of hydrogen ion concentration, temperature and surfactant concentration.

The plots of $^{01}k_{obs}$ versus $[A]_0$ are found to be linear passing through origin (vide Figs. 1 a,b,c and 3 a,b,c) under all conditions in the absence of surfactant as predicted by equation (12). The plots of ^{02}k versus 1/[H+] are found to be linear (vide Figs. 2 a,b,c and 4 a,b,c) giving a positive intercept which represents $^{02}k_H$ and the slopes give $^{01}k_H$, varifying equation (14).

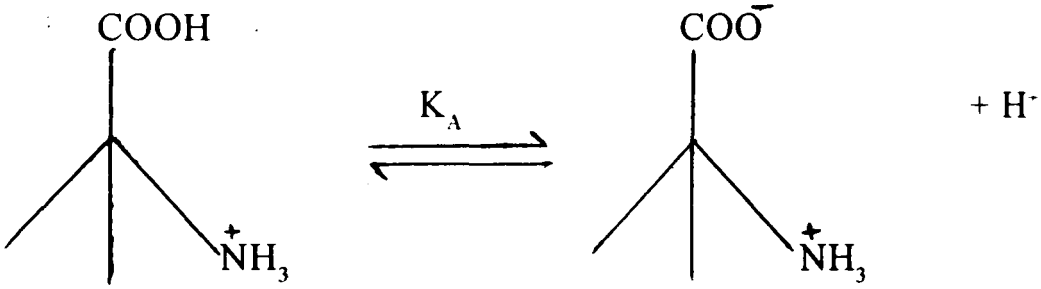
THE STRUCTURAL REPRESENTATION OF DECARBOXYLATION PROCESS MAY BE GIVEN AS BELOW :




(B)
(A)
(OXH)
Followed by step (2) in (A)
(C)
(AH⁻)
(δX)
Followed by step (2) in (A)
(D)
(A)
(δX)
CO₂ +
H-O-H +
RCHO + NH₄

REACTION MECHANISM IN THE PRESENCE OF SURFACTANT :

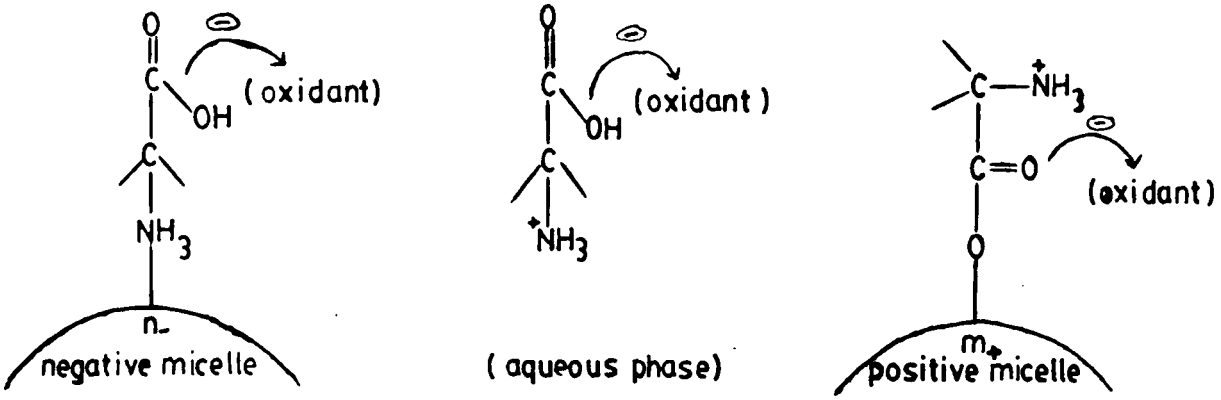
It is observed that the reaction rate in the presence of sodium dodecyl sulfate (SDS) micelles which are negatively charged decreases with increasing concentration of the surfactant. On the other hand, in the presence of cetyl pyridinium chloride (CPC) micelles which are positively cahrged the reaction rate increases with the concentration of surfactant. In the acidity range in which the present investigation has been carried out it is safe to assume that - NH_2 group amino acid is completely protonated whereas, carboxylic group of the amino acids may be partly present in the ionic form. Therefore, so far as substrate is concerned the following species have been taken into consideration.



with this in view, it is expected that the oxidation site is carboxylic group in preference to NH_3 group[17-21].

It is assumed that amino acid forms complex with the micelle, then it is difficult to explain the above observed trends in the reaction rate. It may be remembered that oxidation of amino acid requires the transfer of electron from the active amino acid species to the oxidant species. If

amino acid is bound in the negative environment of micelle through electrostatic interacation between protonated amino group and the micelles, the transfer of electron from such species should be easier in comparison to transfer of electron from protonated amino acid in the aqueous phase. The reaction rate may therefore, increase in the micellar environment. Similarly, in the presence of cationic micelles of cetyl pyridinium chloride protonated amino acid may be considered bound to be micelles through carboxylic group. In this situation the protonated amino group may lie in stern layer. The withdrawal of electron from such intermediate will be difficult and the reaction rate should decreases as shown from models given below :



(a) (b) (c)

(a) Transfer of electron favourable

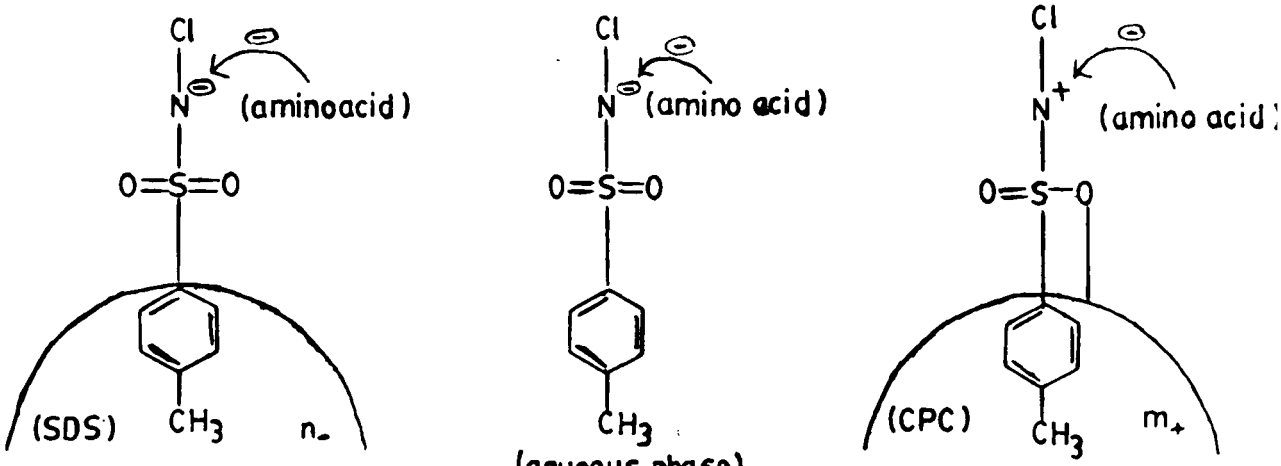
(b) Transfer of electron less favourable

(c) Transfer of electron not favourable

These models clearly indicated that transfer of electron from amino acid bound to negatively charged micelle to the oxidant will be favourable in comparison to transfer of electron from protonated amino acid to the

oxidant in aqueous phase. Similarly, on amino acid bound to positively charged micelle will be poor reducing species. Thus the micelle-substrate complex would predict reaction rate in the presence of SDS to be greater than the reaction rate in the presence of CPC which is contradictory to the observed kinetic behaviour.

In view of the above, it is assumed that the oxidant-micelles complex is more probable species to bring about decarboxylation of amino acid. The oxidant, sodium N-chloro-p-toluenesulphonamide may have better hydrophobic group in comparison to simple aliphatic amino molecule and therefore, its interaction with micelle may be more effective. It is evident that an oxidant present in negatively charged environment will accept electron less favourly as compared to the oxidizing species present in positively charged environment cetyl pyridinium chloride (CPC) micelles. This may be illustrated following models.



(a) (b) (c)

(a) Transfer of electron from amino acid to oxidant-micelle complex not favourable

(b) Transfer of electron less favourable

(c) Transfer of electron more favourable

These models demonstrate that transfer of electron from amino acid to the oxidant-micelle complex is less favourable in the presence of SDS in comparison to electron transfer in the aqueous phase. Also, in the presence of positively charged micelle the oxidizing species may become highly electrophilic and thus reaction rate may increase.

In view of the above discussion, the complex formation of micelles with oxidant has been taken into the consideration to predict kinetic features of decarboxylation of glycine and alanine in the presence of SDS and CPC micelles.

REACTION KINETIC AND MECHANISM IN THE PRESENCE OF SDS :

$$AH^{+} \overset{K_A}{\rightleftharpoons} A + H^{+} \qquad \text{----------} \qquad (1)$$

$$OXH \overset{K_O}{\rightleftharpoons} \bar{O}\bar{X} + H^{+} \qquad \text{----------} \qquad (2)$$

$$\bar{O}\bar{X} + S^{n-} \overset{K_{OS}}{\rightleftharpoons} (OXS)^{n-} \qquad \text{----------} \qquad (3)$$

$$OXH + S^{n-} \overset{K'_{OS}}{\rightleftharpoons} (OXHS)^{n-} \qquad \text{----------} \qquad (4)$$

$$A + OXH \xrightarrow{k_1} \text{-------} \qquad \text{----------} \qquad (5)$$

$$A + \bar{O}\bar{X} \xrightarrow{k_2} \text{-------} \qquad \text{----------} \qquad (6)$$

$$AH^- + OXH \xrightarrow{k_3} \text{--------} \qquad \text{----------} \qquad (7)$$

$$AH^- + O\bar{X} \xrightarrow{k_4} \text{-------} \qquad \text{----------} \qquad (8)$$

$$A + (OXS)^{n-} \xrightarrow{k'_2} \text{-------} \qquad \text{----------} \qquad (9)$$

$$A + (OXHS)^{n-} \xrightarrow{k'_1} \text{-------} \qquad \text{----------} \qquad (10)$$

K_A, K_O, K_{OS} and K'_{OS} may be defined as

$$K_A = \frac{[A]\,[H^+]}{[AH^+]} \quad ; \qquad K_O = \frac{[O\bar{X}]\,[H^+]}{[OXH]}$$

$$K_{OS} = \frac{[OXS]^{n-}}{[O\bar{X}][S^{n-}]} \qquad \text{and} \qquad K_{OS} = \frac{[OXHS]^{n-}}{[OXH]\,[S^{n-}]}$$

The ratio of K_{OS} / K'_{OS} may be given as

$$\frac{K_{OS}}{K'_{OS}} = \frac{[OXS]^{n-}}{[O\bar{X}][S^{n-}]} \cdot \frac{[OXH]\,[S^{n-}]}{[OXHS]^{n-}}$$

$$= \frac{[OXS]^{n-}}{[OXHS]^{n-}} \cdot \frac{[H^+]}{K_O} \qquad \text{----------} \qquad (11)$$

Using the mass balanced equation for amino acid concentration as shown earlier,

$$[A]_0 = [A] + [AH^+]$$

$$= [A]\left(1 + \frac{[H^+]}{K_A}\right)$$

$$= \frac{[A]}{K_A}(K_A + [H^+])$$

$$[A]_0 = \frac{[A]}{K_A} \cdot D \qquad \text{----------} \qquad (12)$$

Also

$$[A]_0 = \frac{[AH^+]}{[H^+]} \cdot D \qquad \text{----------} \qquad (13)$$

where $D = (K_A + [H^+])$

Similarly using the mass balanced equation for the oxidant concentration, the concentration of active oxidizing species may be obtained in terms of $[OX]_T$.

$$[OX]_T = [\bar{OX}] + [OXH] + [OXS]^{n-} + [OXHS]^{n-}$$

$$= [\bar{OX}]\left(1 + \frac{[H^+]}{K_O} + K_{OS}[S^{n-}] + K_{OS}\frac{[H^+]}{K_O}[S^{n-}]\right)$$

$$= \frac{[\bar{OX}]}{K_O}(K_O + [H^+] + K_O K_{OS}[S^{n-}] + K_{OS}[H^+][S^{n-}])$$

$$\text{----------} \qquad (14)$$

$$[OX]_T = \frac{[OXH]}{[H^+]} (K_O + [H^+] + K_O K_{OS} [S^{n-}] + K'_{OS} [H^+] [S^{n-}]) \quad \text{----------} \quad (15)$$

$$= \frac{[OXS]^{n-}}{K_O K_{OS} [S^{n-}]} (K_O + [H^-] + K_O K_{OS} [S^{n-}] + K'_{OS} [H^+] [S^{n-}])$$

$$\text{----------} \quad (16)$$

$$= \frac{[OXHS]^{n-}}{K_{OS} [H^+] [S^{n-}]} (K_O + [H^-] + K_O K_{OS} [S^{n-}] + K'_{OS} [H^+] [S^{n-}])$$

$$\text{----------} \quad (17)$$

where $D' = (K_O + [H^+] + K_O K_{OS} [S^{n-}] + K'_{OS} [H^+] [S^{n-}])$

simplifying DD', we get

$$DD' = (K_A + [H^+]) (K_O + [H^+] + K_O K_{OS} [S^{n-}] + K'_{OS} [H^+] [S^{n-}])$$

$$= (K_A K_O + K_A K_O K_{OS} [S^{n-}]) + (K_A [H^+] + K_O [H^+]$$

$$+ K_A K'_{OS} [H^+][S^{n-}] + [H^-]^2 + K_O K_{OS} [H^+][S^{n-}]$$

$$+ K'_{OS} [H^+]^2 [S^{n-}])$$

neglected $[H^+]^2$, and assuming $K_A K_O$ and $K_A K_O K_{OS} [S^{n-}]$ to be less than one.

$$D.D' \approx \{(K_A + K_O) + (K_A K'_{OS} + K_O K_{OS}) [S^{n-}]\} [H^+]$$

$$\approx D_S [H^+]$$

where

$$D_S = \{(K_A + K_O) + (K_A K'_{OS} + K_O K_{OS}) [S^{n-}]\} \quad \text{----------} \quad (18)$$

The rate law may be obtained as below :

$$\text{reaction rate} = (k_1[OXH] + k_2[\overline{OX}] + k'_2[OXS]^{n-} + k'_1[OXHS]^{n-})[A]$$

$$+ (k_3[OXH] + k_4[\overline{OX}])[AH^+]$$

$$= (k_1 K_A [H^+] + k_2 K_A K_O + k'_2 K_A K_O K_{OS}[S^{n-}]$$

$$+ k'_1 K_A K'_{OS}[H^+][S^{n-}]) \frac{[A]_0 [OX]_T}{D_S [H^+]}$$

$$+ (k_3[H^+] + k_4 K_O) \cdot \frac{[A]_0 [H^+][OX]_T}{D_S [H^+]}$$

$$= (k_1 K_A + \frac{k_2 K_A K_O}{[H^+]} + \frac{k'_2 K_A K_O K_{OS}[S^{n-}]}{[H^+]}$$

$$+ k'_1 K_A K'_{OS}[S^{n-}] + k_3[H^+] + k_4 K_O) \frac{[A]_0 [OX]_T}{D_S}$$

---------- (19)

Putting the value of D_S from equation (18)

$$\text{reaction rate} = \{(k_1 K_A + k_4 K_O + k'_1 K_A K'_{OS}[S^{n-}])$$

$$+ \frac{k_2 K_A K_O + k'_2 K_A K_O K_{OS}[S^{n-}]}{[H^+]}\} \frac{[A]_0 [OX]_T}{(K_A + K_O) + (K_A K'_{OS} + K_O K_{OS})[S^{n-}]}$$

---------- (20)

Assuming k3 << 1

(a) At constant SDS the equation (20) may be simplified to

$$\text{reaction rate} = \{^{-2}k_H + {}^{-1}k_H \cdot \frac{1}{[H^+]}\} [A]_0 [OX]_T$$

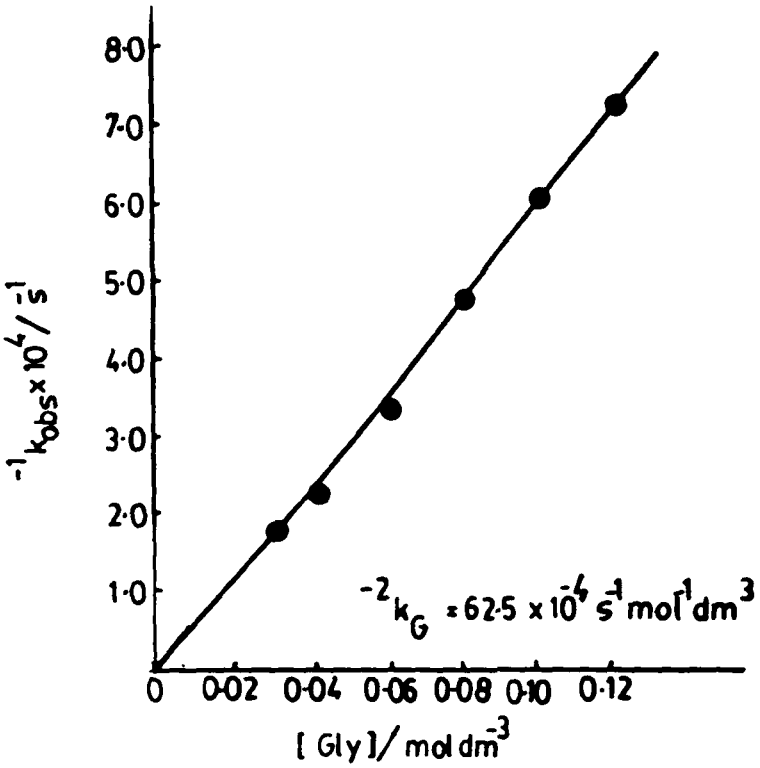


Figure 5a: Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp = 30°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3},

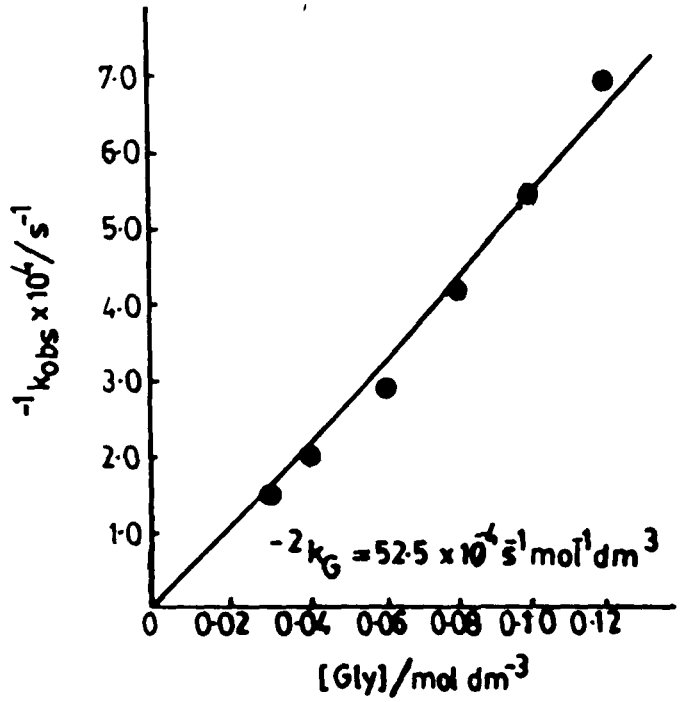


Figure 5b: Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp = 30°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3} [SDS] = 0·02 mol dm^{-3}

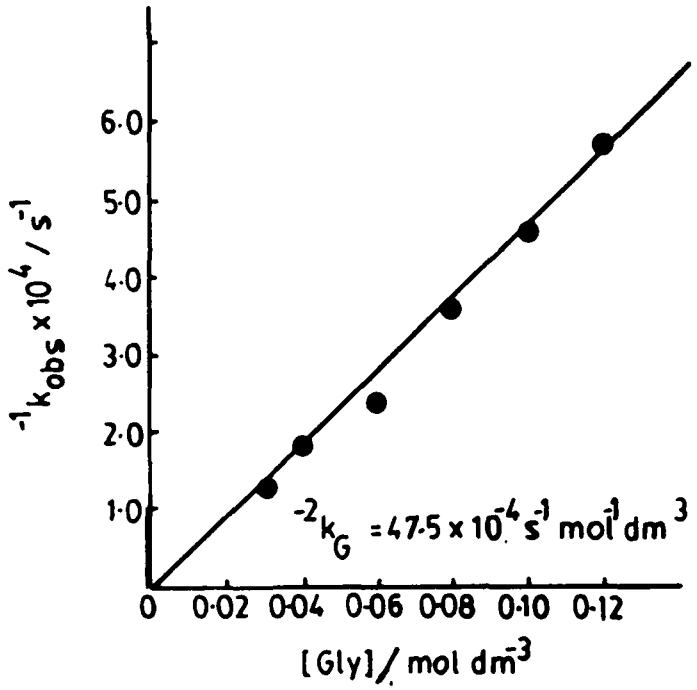


Figure 5c: Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp. = 30°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·03 mol dm^{-3}

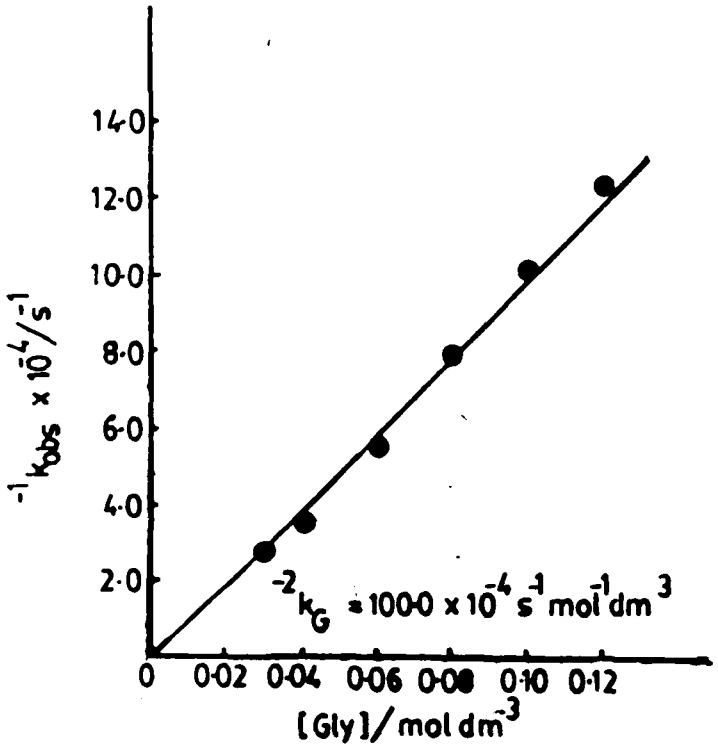


Figure 6a: Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp. = 35°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

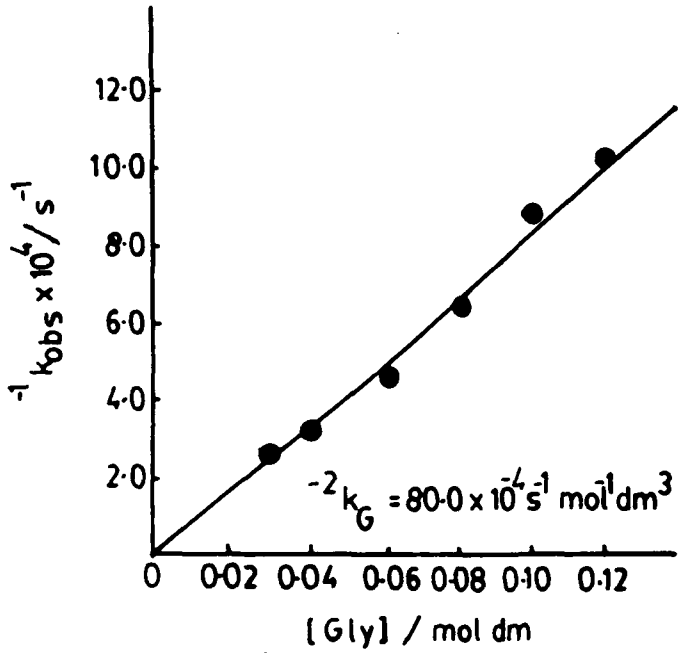


Figure 6b: Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp = 35°C, [H^+] = 0·05 mol dm^{-3}, [CAT] = 2 x 10 mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·02 mol dm^{-3}

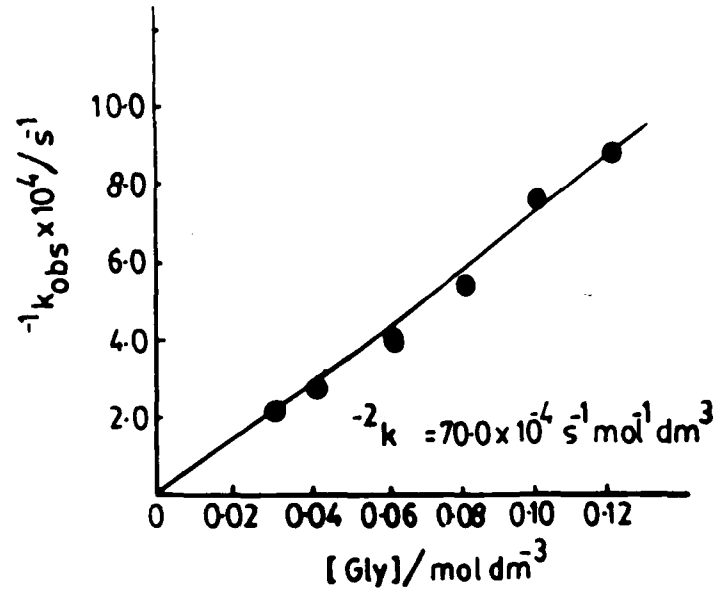


Figure 6c : Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp = 35°C, [H^+] = 0·05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·03 mol dm^{-3}.

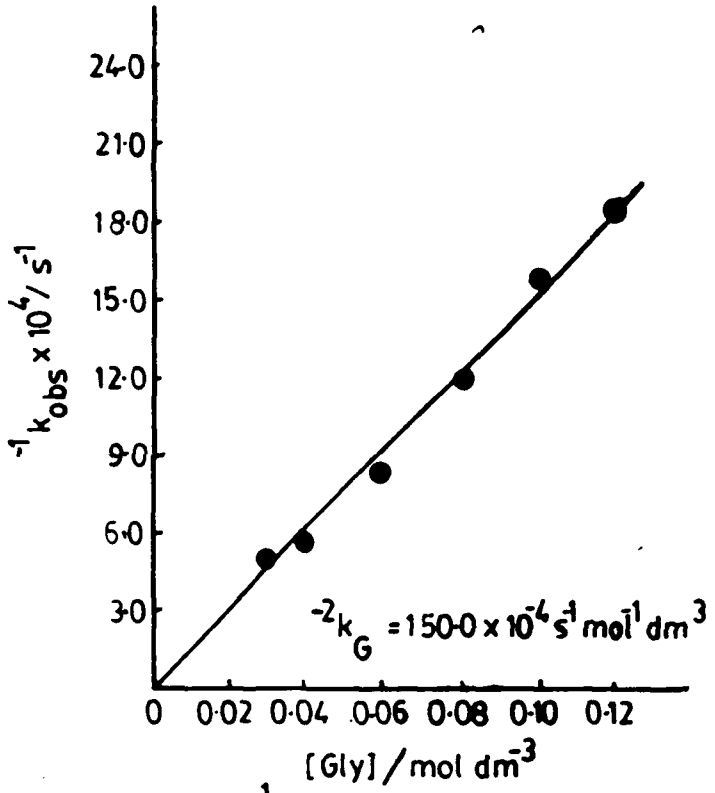


Figure 7a: Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp = 40°C, $[H^+] = 0{\cdot}05$ mol dm^{-3}, $[CAT] = 2 \times 10^{-3}$ mol dm^{-3},

$\mu = 0{\cdot}20$ mol dm^3, [SDS] = 0·01 mol dm^3

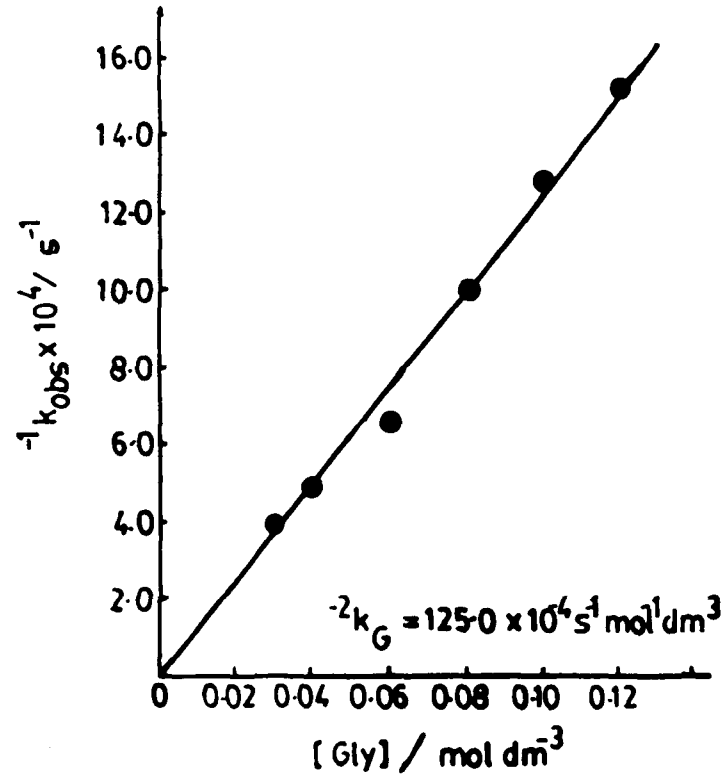


Figure 7b Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp. = 40°C, $[H^+] = 0{\cdot}05$ mol dm^{-3}, $[CAT] = 2 \times 10^{-3}$ mol dm^{-3},

$\mu = 0{\cdot}20$ mol dm^{-3}, [SDS] = 0·02 mol dm^{-3}

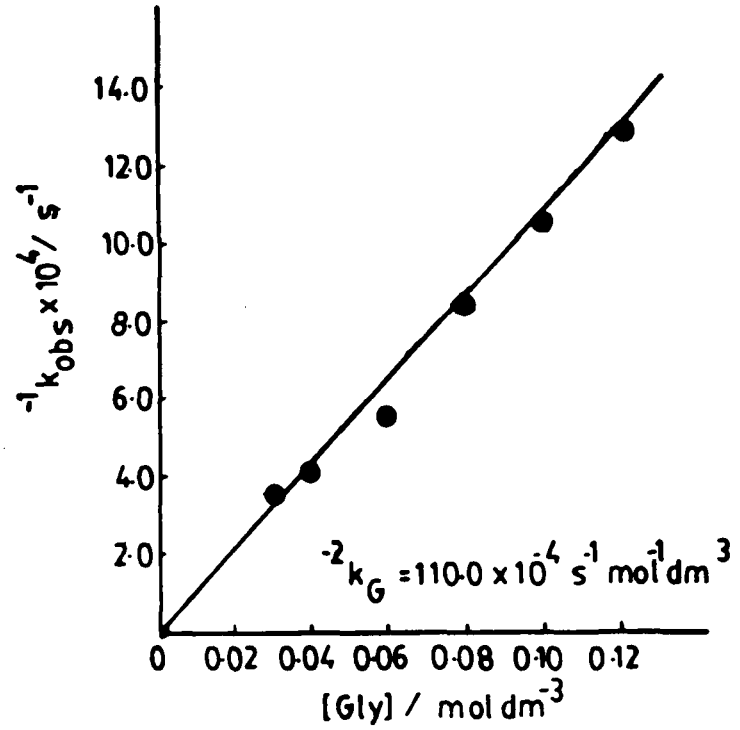


Figure 7c : Plot of $^{-1}k_{obs}$ VS [Gly] in the presence of SDS

Temp = 40°C , [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·03 mol dm^{-3}

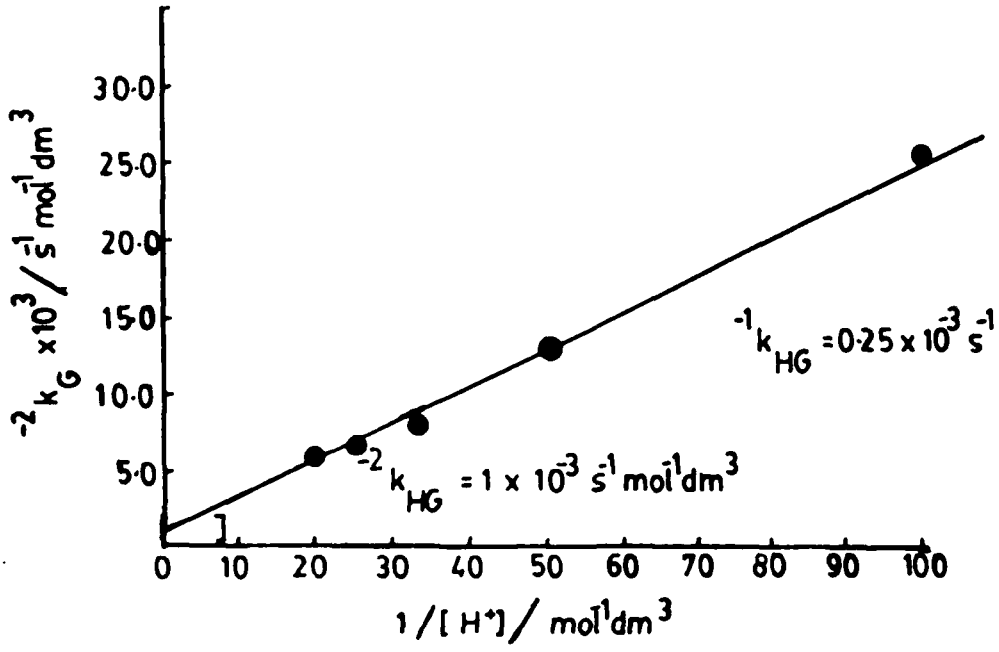


Figure 8a : Plot of $^{-2}k_G$ VS 1/[H$^+$] in the presence of SDS

Temp = 30°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

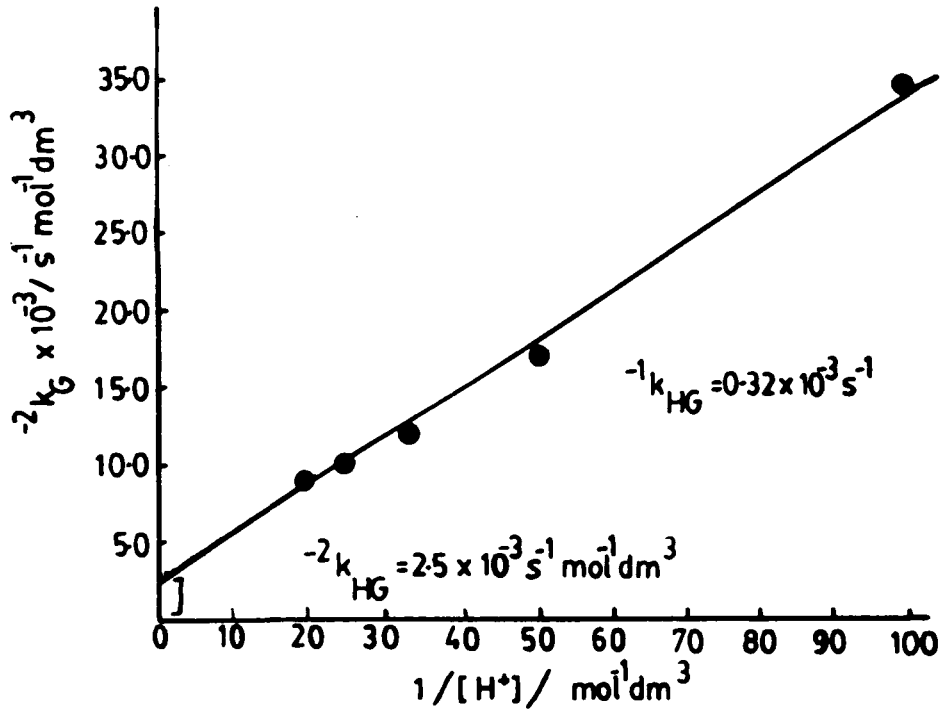


Figure 8b: Plot of $^{-2}k_G$ VS $1/[H^+]$ in the presence of SDS

Temp = 35°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2 × 10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}.

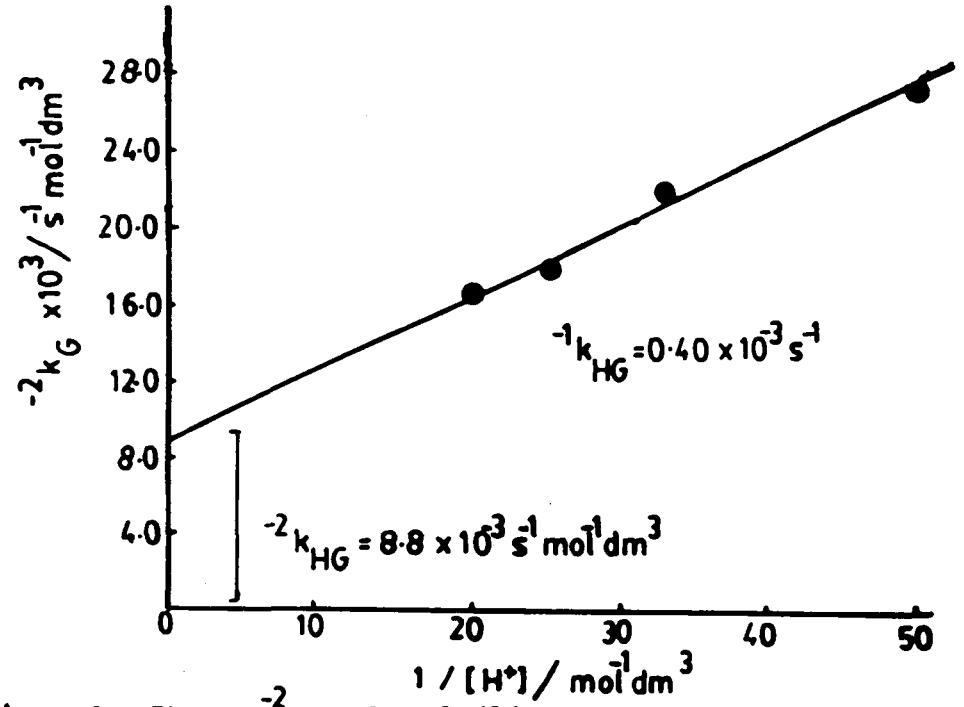


Figure 8c: Plot of $^{-2}k_G$ VS $1/[H^+]$ in the presence of SDS

Temp = 40°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2 × 10^{-3} mol dm^{-3}

μ = 0·20 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

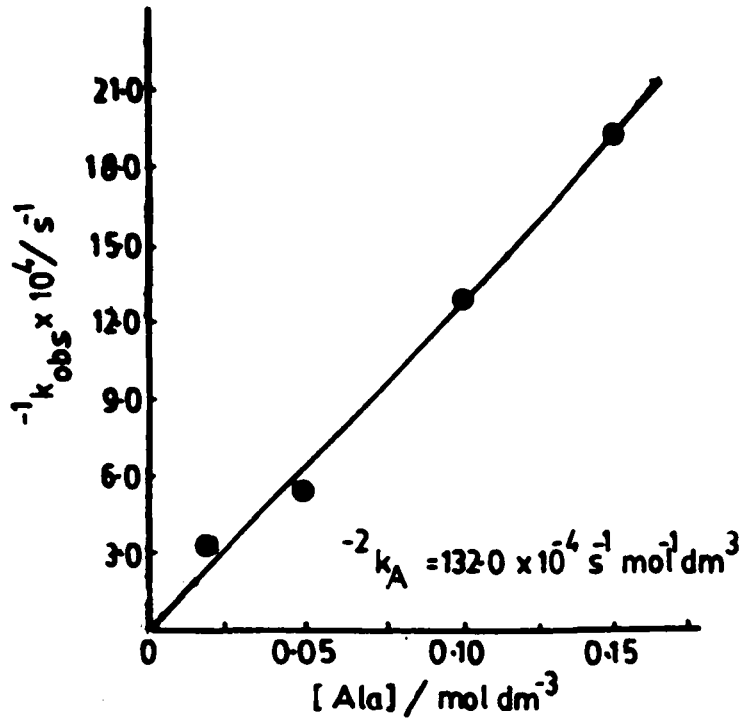


Figure 9a: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS
Temp=30°C , [H^+]=0·05 mol dm^3,[CAT]=2 x 10^3 mol dm^3,
μ=0·15 mol dm^{-3}, [SDS]=0·01 mol dm^{-3}

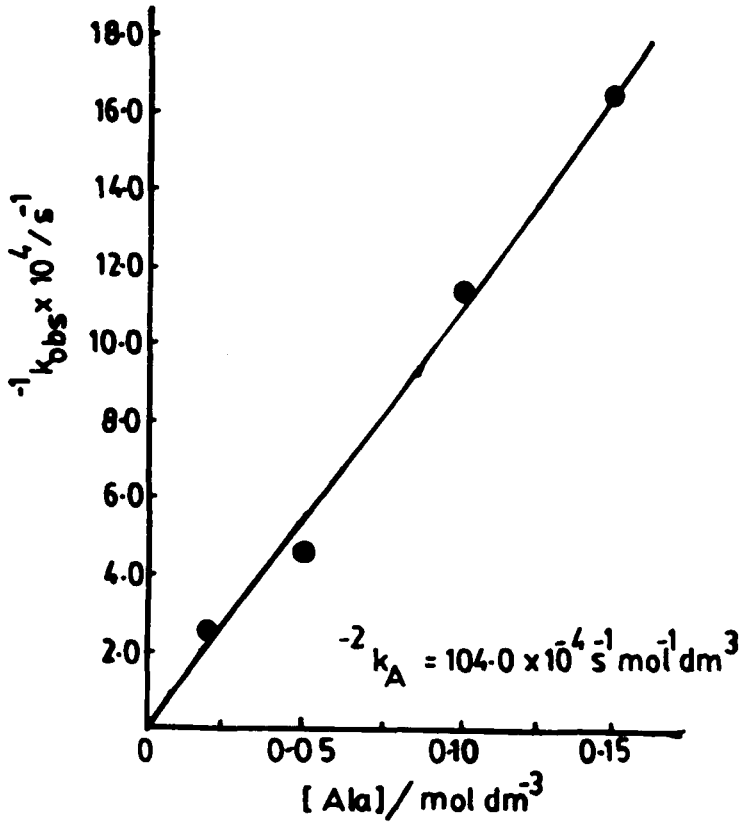


Figure 9b: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS
Temp=30°C , [H^+]=0·05 mol dm^{-3}, [CAT]=2 x 10^{-3} mol dm^{-3},
μ=0·15 mol dm^{-3}, [SDS]=0·02 mol dm^{-3}

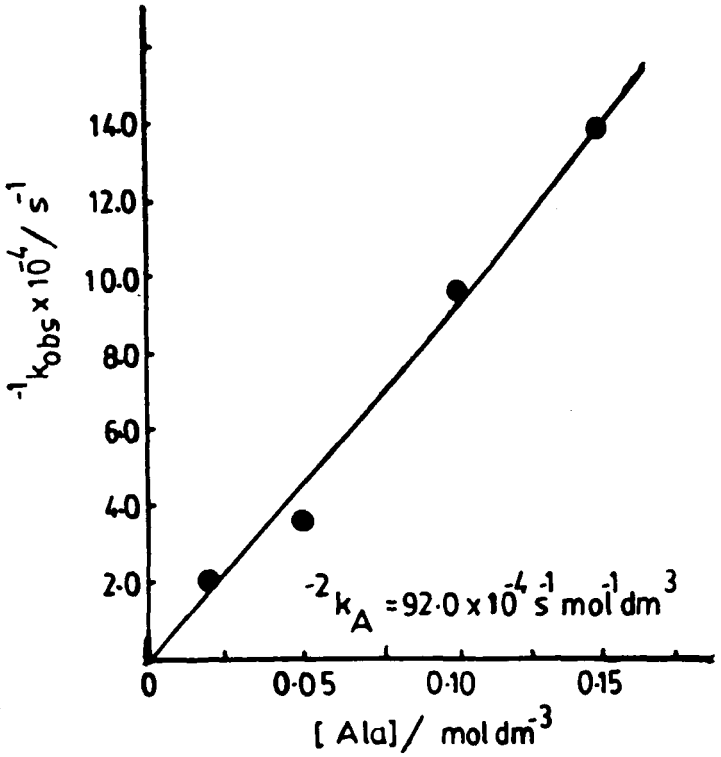


Figure 9c: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS

Temp = 30°C, $[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0.15 mol dm^{-3}, [SDS] = 0.03 mol dm^{-3}

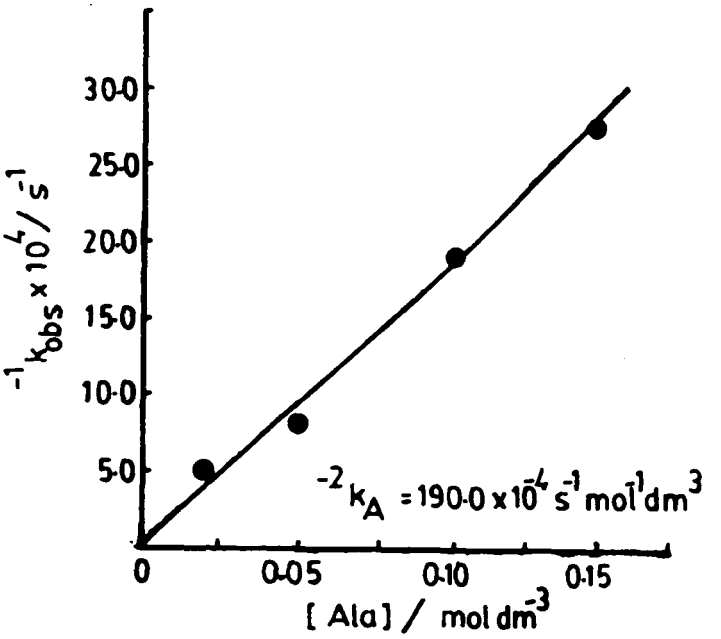


Figure 10a: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS

Temp = 35°C, $[H^+]$ = 0.05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0.15 mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}

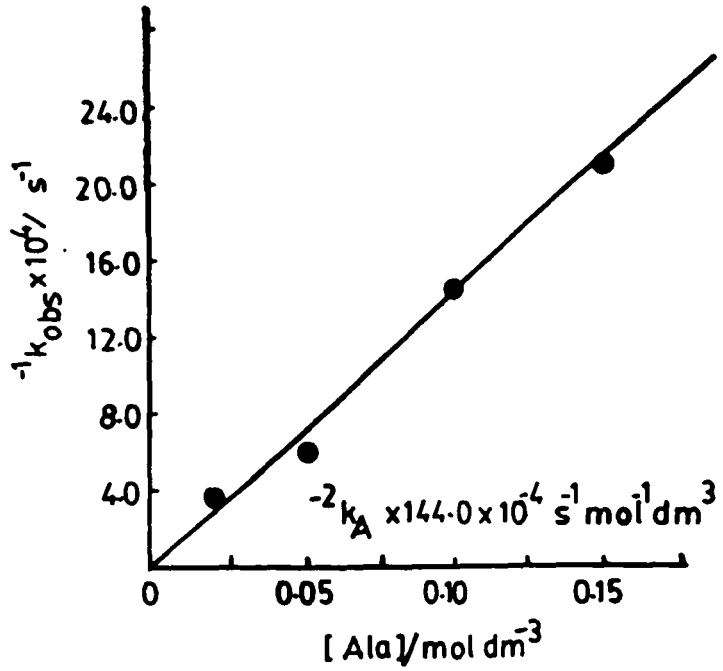


Figure 10 b: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS
Temp = 35°C, [H$^+$] = 0.05 mol dm^{-3}, [CAT] = 2 x 10 mol dm^{-3},
μ = 0.15 mol dm^{-3}, [SDS] = 0.02 mol dm^{-3}

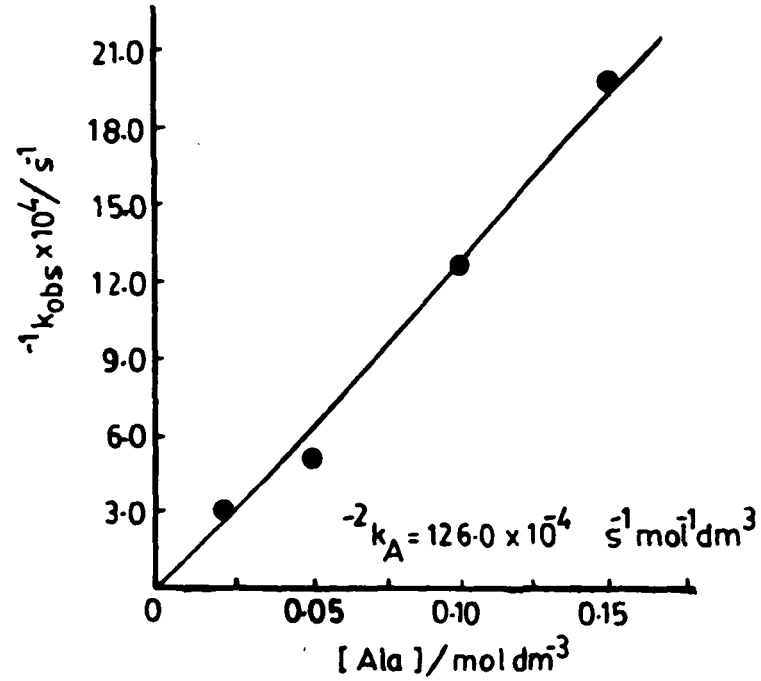


Figure 10 c : Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS
Temp = 35°C, [H$^+$] = 0.05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},
μ = 0.15 mol dm^{-3}, [SDS] = 0.03 mol dm^{-3}

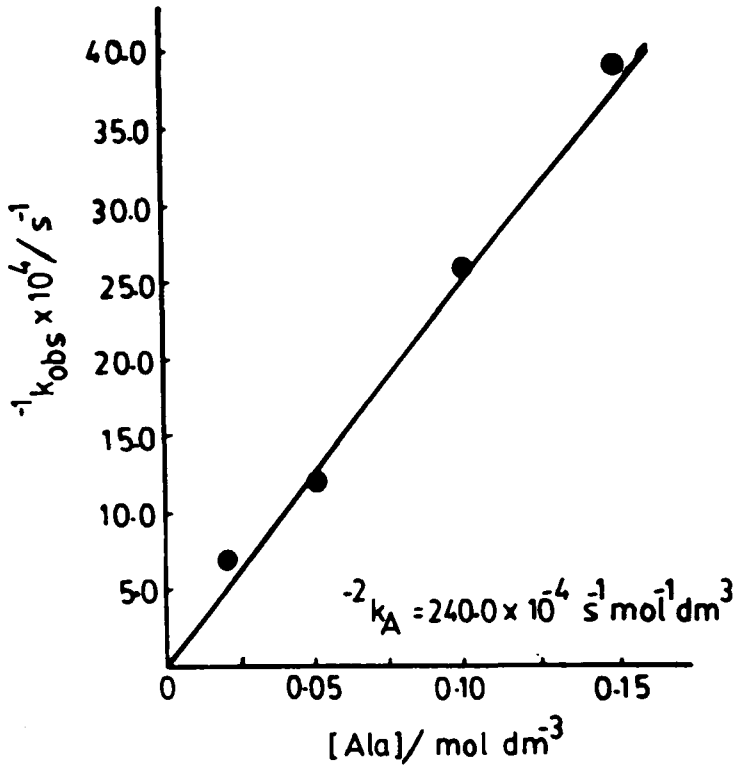


Figure 11a : Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS

Temp = 40° C, [H^+] = 0.05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0.15 mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}

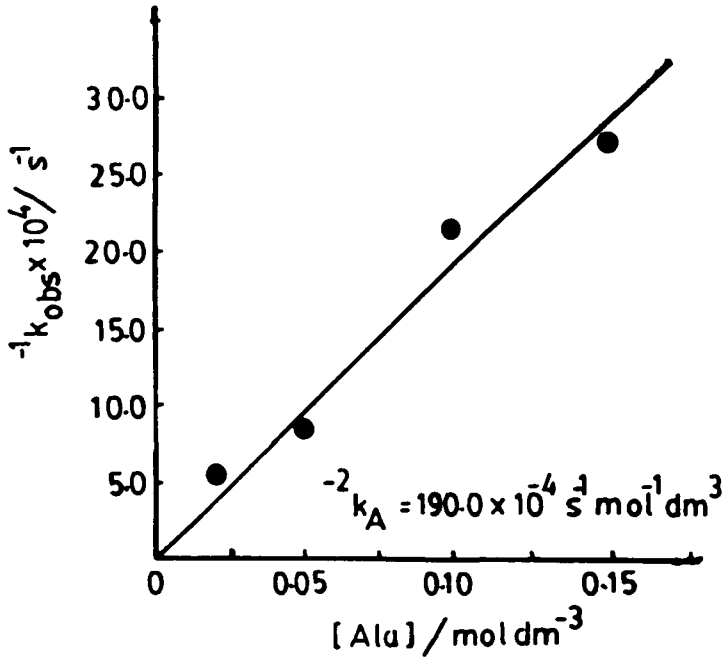


Figure 11b: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence of SDS

Temp = 40° C, [H^+] = 0.05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0.15 mol dm^{-3}, [SDS] = 0.02 mol dm^{-3}

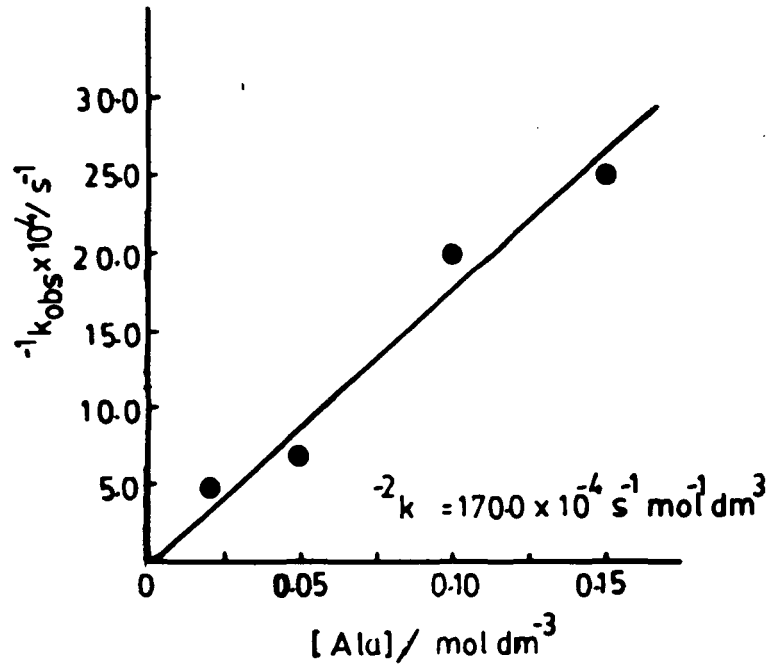


Figure 11c: Plot of $^{-1}k_{obs}$ VS [Ala] in the presence SDS
Temp = 40°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·15 mol dm^{-3}, [SDS] = 0·03 mol dm^{-3}

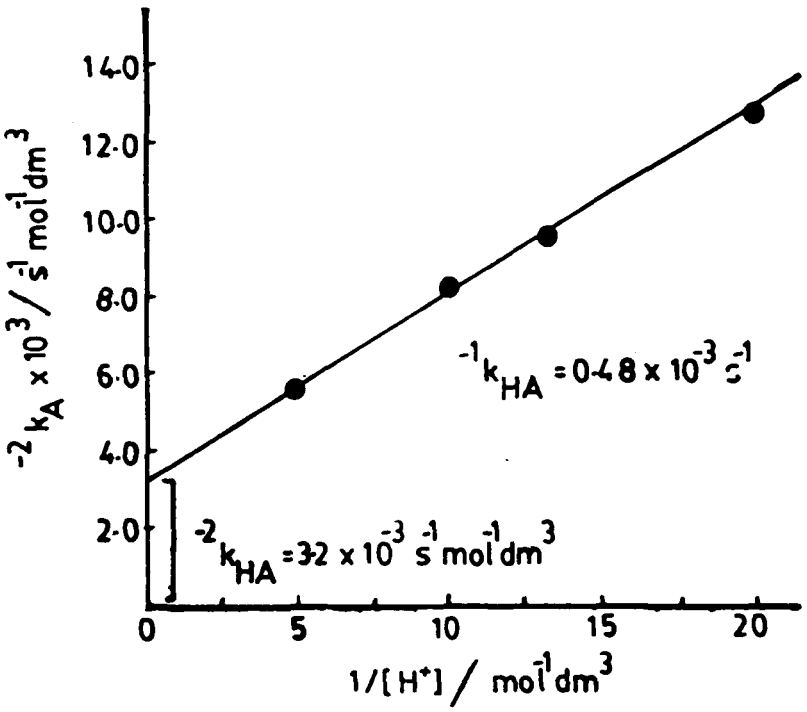


Figure 12a: Plot of $^{-2}k_A$ VS 1/[H$^+$] in the presence of SDS
Temp = 30°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·15 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

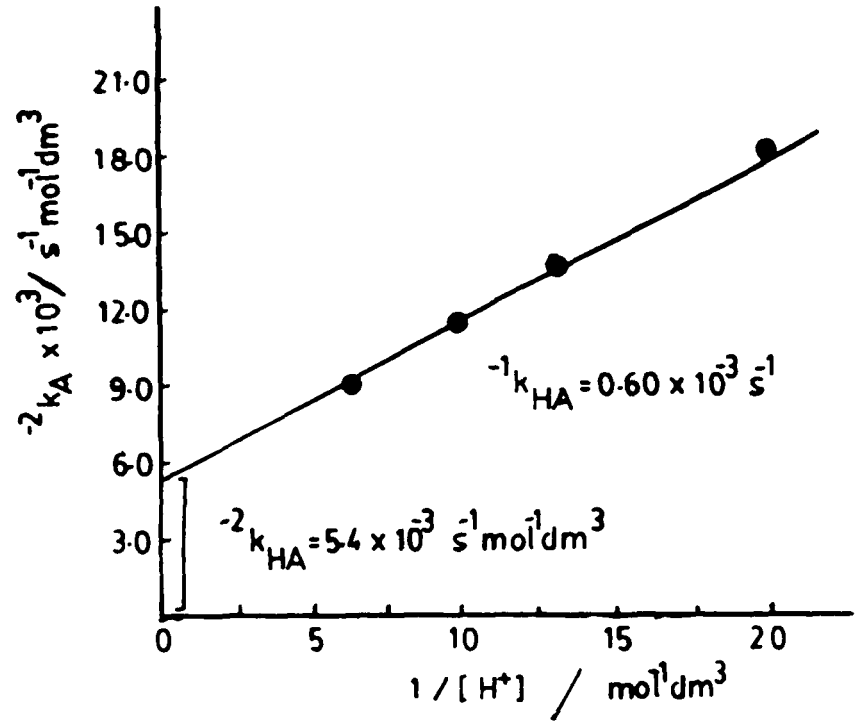


Figure 12b: Plot of $^{-2}k_A$ VS $1/[H^+]$ in the presence of SDS

Temp = 35°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

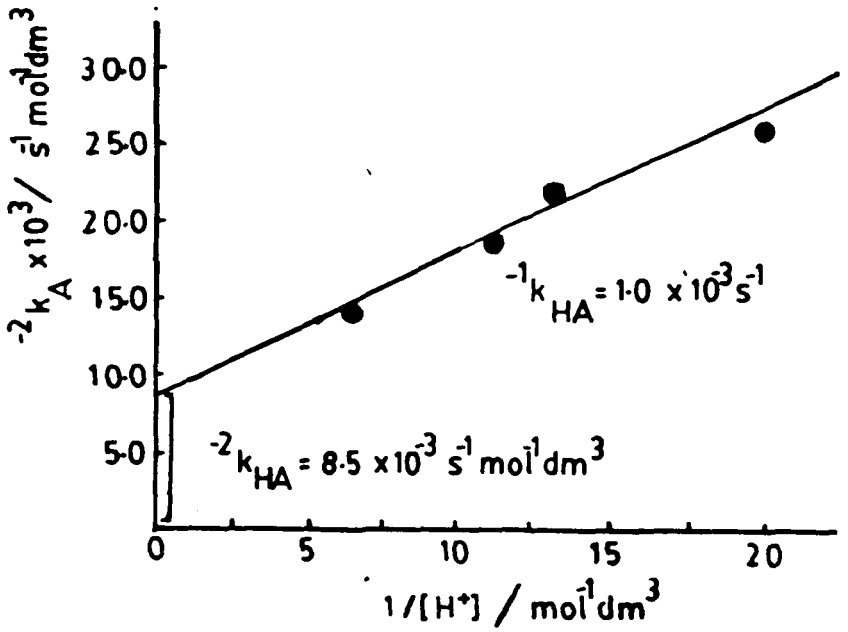


Figure 12c: Plot of $^{-2}k_A$ VS $1/[H]$ in the presence of SDS

Temp = 40°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [SDS] = 0·01 mol dm^{-3}

$$= {}^{-2}k\ [A]_0\ [OX]_T = {}^{-1}k_{obs}\ [OX]_T \quad \text{----------} \quad (21)$$

$${}^{-2}k = \{{}^{-2}k_H + {}^{-1}k_H \cdot \frac{1}{[H^+]}\} \quad \text{----------} \quad (22)$$

The plots between ${}^{-1}k_{obs}$ versus $[A]_0$ are linear and pass through the origin at different conditions (vide Figs. 5 a,b,c to 7 a,b,c and 9 a,b,c to 11 a,b,c).

where

$${}^{-2}k_H = \frac{(k_1K_A + k_4K_O + k'_1K_AK'_{OS}[S^n-])}{(K_A+K_O)+(K_AK'_{OS}+K_OK_{OS})[S^n-]}$$

${}^{-2}k_H$ represents second order rate constant in the presence of SDS associated with reaction path not affected by $[H^+]$.

and

$${}^{-1}k_H = \frac{K_A(k_2K_O + k'_2K_OK_{OS}[S^n-])}{(K_A+K_O)+(K_AK'_{OS}+K_OK_{OS})[S^n-]}$$

${}^{-1}k_H$ represents the first order rate constant in the presence of SDS associated with reaction path adversely affected by $[H^+]$.

The above equation stands verified as plots between ${}^{-2}k$ versus $1/[H^+]$ are found to be linear at different temperatures (vide Figs. 8 a,b,c and 12 a,b,c). From the slopes of these plots, the first order rate constant ${}^{-1}k_H$ showing dependence on hydrogen ion concentration were calculated at different temperatures whereas, from the intercepts, the second order rate constants signifying the hydrogen ion independent reaction path were also calculated at different temperatures.

(b) At constant $[H^+]$ the equation (22) for the ^{-2}k may be rearranged to give,

$$^{-2}k = \frac{k_1K_A + k_4K_O + k'_1K_AK'_{OS}[S^n-]}{(K_A+K_O)+(K_AK'_{OS}+K_OK_{OS})[S^n-]} + \frac{k_2K_A K_O + k'_2K_A K_OK_{OS}[S^n-]}{(K_A+K_O)+(K_AK'_{OS}+K_OK_{OS})[S^n-]} \cdot \frac{1}{[H^+]}$$

$$^{-2}k = \frac{(k_1K_A + k_4K_O + k_2K_AK_O/[H^+])\cdot 1/K_A+K_O}{(1+\frac{K_AK'_{OS}+K_OK_{OS}}{K_A+K_O}[S^n-])} + \frac{(\frac{k'_2K_AK_OK_{OS}/[H^+]+k'_1K_AK'_{OS}}{K_AK'_{OS}+K_OK_{OS}})\frac{K_AK'_{OS}+K_OK_{OS}}{K_A+K_O}[S^n-]}{(1+\frac{K_AK'_{OS}+K_OK_{OS}}{K_A+K_O}[S^n-])}$$

$$^{-2}k = \frac{^{02}k}{1+K_-[S^n-]} + \frac{^{-2}k_mK_-[S^n-]}{1+K_-[S^n-]} \qquad (23)$$

where $^{02}k = (k_1K_A + k_4K_O + k_2K_AK_O/[H^+])\ 1/K_A + K_O$;

$$^{-2}k_m = \frac{k'_2K_AK_OK_{OS}/[H^+]+k'_1K_AK'_{OS}}{K_AK'_{OS}+K_OK_{OS}}$$

and

$$K_- = \frac{K_AK'_{OS}+K_OK_{OS}}{K_A+K_O}$$

The **Menger**[22] equation may be obtained by substracting ^{02}k from both sides in equation (23).

$$^{-2}k - {}^{02}k = \frac{^{02}k}{1 + K_{-}[S^{n-}]} + \frac{^{-2}k_m K_{-}[S^{n-}]}{1 + K_{-}[S^{n-}]} - {}^{02}k$$

$$= \frac{^{02}k + {}^{-2}k_m K_{-}[S^{n-}] - {}^{02}k - {}^{02}k K_{-}[S^{n-}]}{1 + K_{-}[S^{n-}]}$$

$$^{-2}k - {}^{02}k = \frac{(^{-2}k_m - {}^{02}k) K_{-}[S^{n-}]}{1 + K_{-}[S^{n-}]}$$

Taking the reciprocal of the above equation,

$$\frac{1}{^{-2}k - {}^{02}k} = \frac{1}{^{-2}k_m - {}^{02}k} + \frac{1}{^{-2}k_m - {}^{02}k} \cdot \frac{1}{K_{-}[S^{n-}]}$$

or

$$\frac{1}{^{02}k - {}^{-2}k} = \frac{1}{^{02}k - {}^{-2}k_m} + \frac{1}{^{02}k - {}^{-2}k_m} \cdot \frac{1}{K_{-}[S^{n-}]} \quad \text{------ (24)}$$

The concentration of micelles, $[S^{n-}]$, may be obtained using **Shinoda** and **Hutchinson**[23] assumption that above cmc the concentration of unassociated surfactant remains constant, giving

$$[S^{n-}] = \frac{D_o - cmc}{N}$$

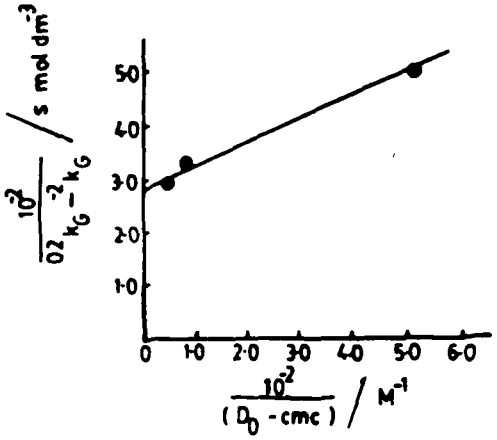


Figure 13a: Temp = 30°C

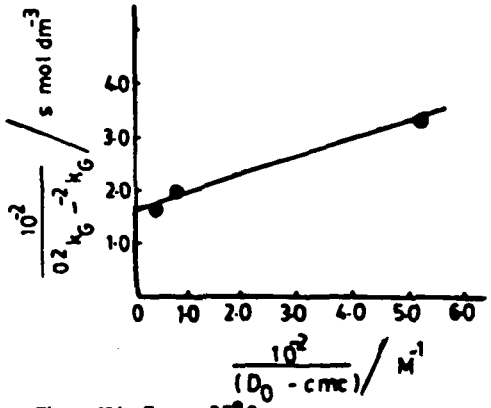


Figure 13b: Temp = 35°C

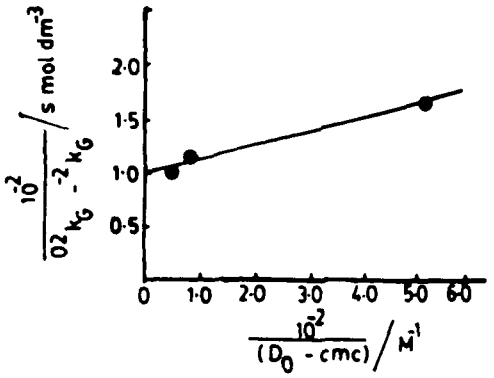


Figure 13c: Temp = 40°C

Figures 13a,b,c: Plots of $\frac{1}{O2_{k_G} - {}^{-2}k_G}$ VS $\frac{1}{(D_0 - cmc)}$ at different temperatures

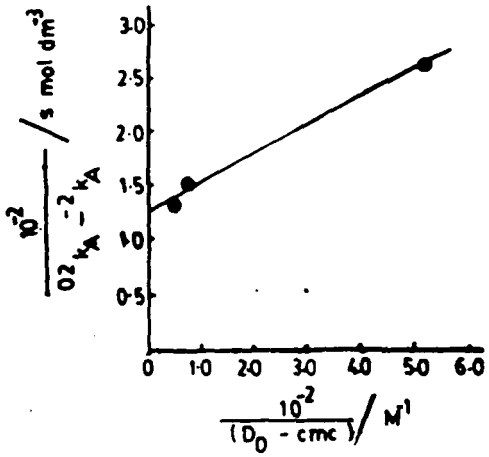


Figure 14a : Temp = 30°C

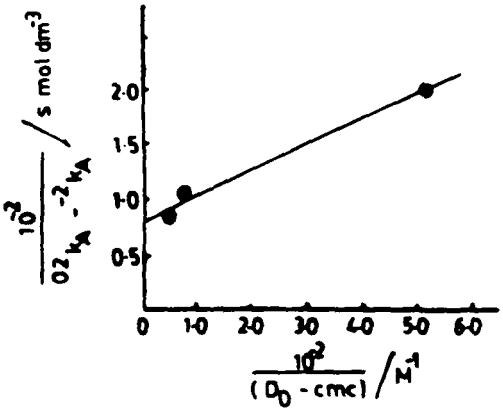


Figure 14b : Temp = 35°C

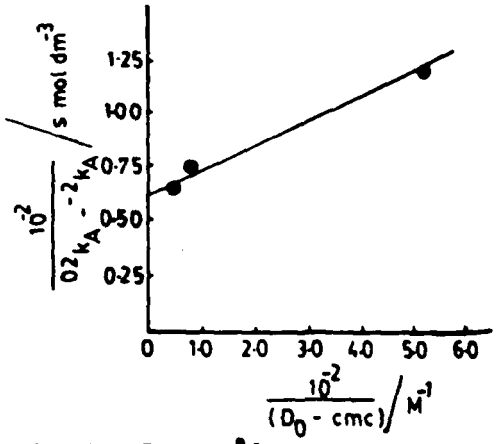


Figure 14c : Temp = 40°C

Figures 14a,b,c : Plots of $\frac{1}{{}^{0}_{2}k_A - {}^{2}k_A}$ VS $\frac{1}{(D_0 - cmc)}$ at different temperatures

TABLE-5 : Temperature dependence of $^{-2}k_m$ and $K_.$ for glycine and alanine in the presence of SDS.

Temps. (°C)	Glycine		Alanine	
	$^{-2}k_{mG}$ x10^3/s^{-1} mol^{-1} dm^3	$K_./10^4$ mol^{-1} dm^3	$^{-2}k_{mA}$ x10^3/s^{-1} mol^{-1} dm^3	$K_./10^4$ mol^{-1} dm^3
30	4.7	3.8	9.0	2.8
35	6.7	2.8	11.5	2.2
40	11.0	4.9	15.8	2.9

Where D_o is the concentration of SDS used and N represent the aggregate number. The value of cmc for SDS has been taken as 8.1×10^{-3} which is only marginally affected by temperature from 25° to 40°C [24].

The above equation takes the form,

$$\frac{1}{{}^{02}k - {}^{-2}k} = \frac{1}{{}^{02}k - {}^{-2}k_m} + \frac{1}{{}^{02}k - {}^{-2}k_m} \cdot \frac{N}{K_-} \cdot \frac{1}{(D_o\text{-cmc})} \qquad \text{------- (25)}$$

This equation has been tested by plots of $1/{}^{02}k - {}^{-2}k$ versus $1/(D_o\text{-cmc})$ which is found to be linear (vide Figs. 13 a,b,c and 14 a,b,c) and the reciprocal of the intercept gives $({}^{02}k - {}^{-2}k)$ from which values of ${}^{-2}k_m$ at different temperatures have been calculated and its activation parameters have also been evaluated. The ratio of slope versus intercept of the above equation gives the value of N/K. Using the aggregate number for SDS, N=62.0 [25], the value of K_- has been also obtained (Table 5). It may be pointed out that K_- in the above reaction mechanism does not represent simple binding parameter between oxidant and the micelles rather it is a complex function of K_{os} and K'_{os} representing oxidant surfactant equilibria.

OXIDATIVE DEGRADATION OF GLYCINE IN THE PRESENCE OF CPC :

As discussed earlier, the oxidation rate of glycine as well as that of alanine is enhanced in the presence of CPC. The most significant difference in comparison to the oxidation in the presence of SDS is that CPC-catalyzed reaction does not follow Menger's equation. It appears that pre-micellar aggregates including the monometer play an important role by complexing through electrostatic interaction with anionic oxidizing species. It is further observed that the reaction follows a modified Menger equation which is adequately supported by the reaction mechanism as given below :

Reaction Mechanism and Rate Law :

$$AH^+ \overset{K_A}{\rightleftharpoons} A + H^- \quad \text{---------- (1)} \quad K_A/[H^+] = [A]/[AH^+]$$

$$OXH \overset{K_O}{\rightleftharpoons} \bar{OX} + H^+ \quad \text{---------- (2)} \quad K_O/[H^+] = [\bar{OX}]/[OXH]$$

$$OXD \overset{K_d}{\rightleftharpoons} \bar{OX} + D^+ \quad \text{---------- (3)} \quad K_d/[D^+] = [\bar{OX}]/[OXD]$$

$$OXD + S^{m+} \overset{K_{OS}}{\rightleftharpoons} [OXDS]^{m+} \quad \text{------ (4)} \quad K_{OS} = [OXDS]^{m+}/[OXD][S^{m+}]$$

The total concentration of CPC is represented by $[D_0]$ and concentration premicellar aggregates including monomer is $[D^+]$ and concentration of positively charged micelle is represented by $[S^{m+}]$.

$$[D^+] = [D_0] - [S^{m+}] \qquad \text{---------- (a)}$$

with the assumption that oxidant - surfactant complex concentration is always comparatively low ;

$$A + OXH \xrightarrow{k_1} \text{-------} \qquad \text{---------- (5)}$$

$$A + OX \xrightarrow{k_2} \text{-------} \qquad \text{---------- (6)}$$

$$OXH + AH^+ \xrightarrow{k_3} \text{-------} \qquad \text{---------- (7)}$$

$$OX + AH^+ \xrightarrow{k_4} \text{-------} \qquad \text{---------- (8)}$$

$$A + (OXDS)^{m+} \xrightarrow{k'_5} \text{-------} \qquad \text{---------- (9)}$$

Using the mass balanced equation for amino acid concentration as done earlier.

$$[A]_0 = [A] + [AH^+]$$

$$= [A] (1 + [H^+]/K_A)$$

$$= [A]/K_A (K_A + [H^+])$$

$$= \frac{[A]}{K_A} . D \qquad \text{---------- (10)}$$

also

$$= \frac{[AH^+]}{[H^+]} \qquad \text{---------- (11)}$$

where

$$D = (K_A + [H^-])$$

Using the mass balanced equation for the concentration of oxidant species, the values of oxidizing species may be obtained in terms of $[OX]_T$.

$$[OX]_T = [\overline{OX}]+[OXH]+[OXD]+[OXDS]^{m+}$$

$$= [\overline{OX}] (1+ [H^+]/K_O + [D^-]/K_d + K_{OS} [S^{m+}] [D^+]/K_d)$$

$$= \frac{[\overline{OX}]}{K_d K_O} (K_d K_O + K_d [H^+] + K_O [D^+] + K_O K_{OS}[D^-][S^{m+}]) \quad \text{---- (12)}$$

$$= \frac{[OXH]}{K_d [H^+]} (K_d K_O + K_d [H^+] + K_O [D^+] + K_O K_{OS}[D^-][S^{m+}]) \quad \text{---- (13)}$$

$$= \frac{[OXD]}{K_O[D^+]} (K_d K_O + K_d [H^+] + K_O [D^+] + K_O K_{OS}[D^-][S^{m+}]) \quad \text{---- (14)}$$

$$= \frac{[OXDS]^{m+}}{K_O K_{OS} [D^+][S^{m+}]} (K_d K_O + K_d [H^+] + K_O [D^+] + K_O K_{OS}[D^+][S^{m+}])$$

------- (15)

where

$$D'' = (K_d K_O + K_d [H^+] + K_O [D^+] + K_O K_{OS}[D^+][S^{m+}])$$

simplifying

$$DD'' = (K_A + [H^+]) (K_d K_O + K_d [H^+] + K_O [D^+] + K_O K_{OS}[D^+][S^{m+}])$$

------- (16)

from equation (a), putting the value of $[D^+]= [D_0]-[S^{m+}]$ in equation (16)

$$DD'' = K_A (K_dK_O + K_O [D_0 - S^{m+}] + K_OK_{OS}[D_0-S^{m+}] [S^{m+}])$$

$$+ (K_AK_d + K_dK_O + K_O [D_0-S^{m+}] + K_OK_{OS} [D_0-S^{m+}] [S^{m+}]) [H^+] + ...$$

neglecting $[H^+]^2$ and $[S^{m+}]^2$ and assuming $K_A < 1$ and $K_O < 1$.

$$DD'' \approx (K_AK_d + K_dK_O + K_OK_{OS} [D_0][S^{m+}]) [H^+] \quad \text{----------} \quad (17)$$

$$= D'_S [H^+]$$

where

$$D'_S = (K_AK_d + K_dK_O + K_OK_{OS} [D_0][S^{m+}]) \quad \text{----------} \quad (18)$$

The rate law may be obtained as below :

$$\text{reaction rate} = (k_1 [OXH] + k_2 [\overline{OX}] + k'_5 [OXDS]^{m+}) [A]$$

$$+ (k_3 [OXH] + k_4 [\overline{OX}]) [AH^+]$$

$$= (k_1K_d [H^+] + k_2K_dK_O + k'_5K_OK_{OS}[D_0] [S^{m+}]) \frac{K_A [A]_0 [OX]_T}{D'_S [H^+]}$$

$$+ (k_3K_d [H^+] + k_4 K_O K_d) \frac{[A]_0 [OX]_T [H^+]}{D'_S [H^+]}$$

$$= \{k_1K_AK_d + k_2K_AK_dK_O/[H^+] + K'_5K_AK_OK_{OS} [D_0][S^{m+}]/[H^+]$$

$$+ k_3 K_d [H^+] + k_4K_OK_d\} \frac{[A]_0 [OX]_T}{D'_S} \quad \text{-------} \quad (19)$$

Assuming $k_3 << 1$ and putting the value of D'_S from equation (18) in equation (19).

reaction rate = $\{(k_1K_AK_d + k_4K_OK_d)$

$$+ \frac{k_2K_AK_OK_d+k'_5K_AK_OK_{OS}\,[D_0]\,[S^{m+}]}{[H^+]}\} \quad \frac{[A]_0\,[OX]_T}{K_AK_d+K_OK_d+K_OK_{OS}[D_0][S^{m+}]}$$

reaction rate = $\{(k_1 K_A + k_4K_O)$

$$+ \frac{k_2K_AK_O+k'_5K_AK_OK_{OS}[D_0]\,[S^{m+}]}{[H^+]}\} \quad \frac{K_d\,[A]_0\,[OX]_T}{(K_A+K_O+K_OK'_{OS}[D_0][S^{m+}])K_d}$$

---------- (20)

reaction rate = $^{+2}k_G\,[A]_0\,[OX]_T$

The rate constant, $^{+2}k_G$ may bes expressed as,

$$^{+2}k_G = \{\frac{(k_1 K_A + k_4K_O)}{(K_A+K_O) + K_OK'_{OS}[D_0][S^{m+}]} + \frac{k_2K_AK_O+k'_5K_AK_OK'_{OS}[D_0][S^{m+}]}{(K_A+K_O) + K_OK'_{OS}[D_0][S^{m+}]} \cdot \frac{1}{[H^+]}\}$$

---------- (21)

where

$$K_{OS}/K_d = K'_{OS}$$

At Constant CPC :

Kinetic investigation has been carried out at different hydrogen ion concentrations, keeping constant value of CPC and other parameters. Under this consideration the equation (20), written as

reaction rate = $\{^{+2}k_{HG} + {}^{+1}k_{HG} \cdot 1/[H^+]\}\,[A]_0\,[OX]_T$

$= {}^{+2}k_G\,[A]_0\,[OX]_T = {}^{+1}k_{obs}\,[OX]_T$ ---------- (22)

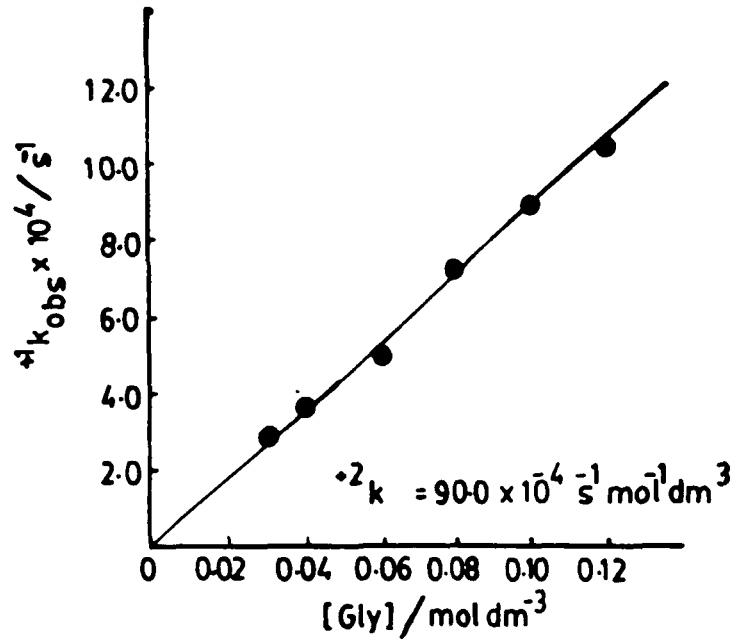


Figure 15a: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp. = 30°C, [H^+] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·002 mol dm^{-3}

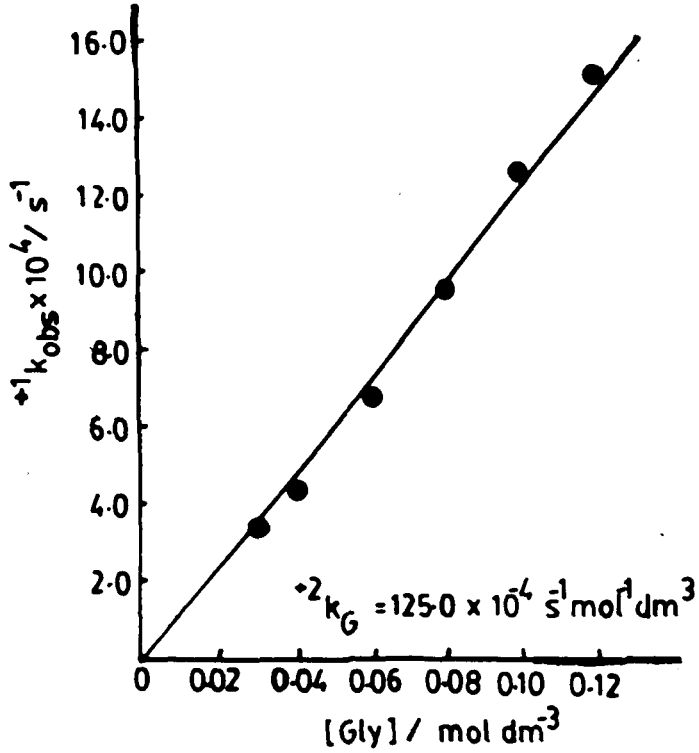


Figure 15b: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp = 30°C, [H^+] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

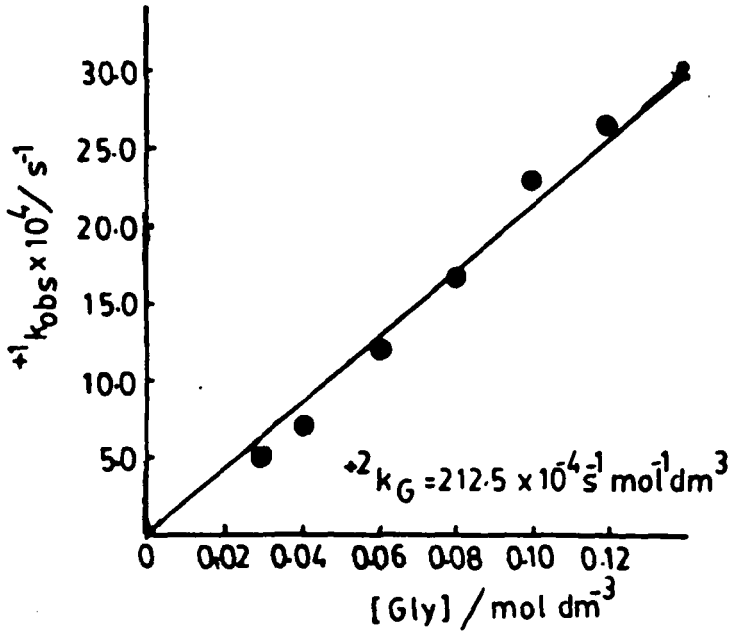


Figure 15c: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp=30°C, [H$^+$]=0·05 mol dm^{-3}, [CAT]=2 x 10^{-3} mol dm^{-3},
μ=0·20 mol dm^{-3}, [CPC]=0·006 mol dm^{-3}

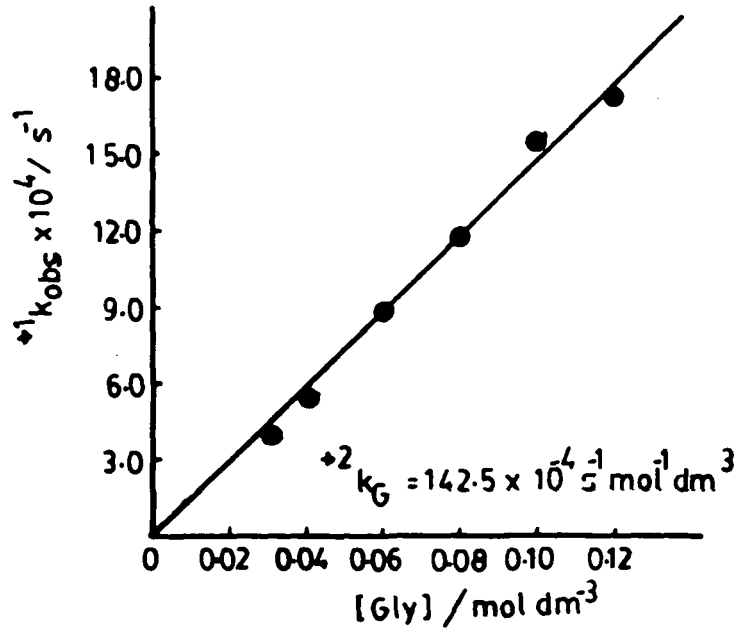


Figure 16a: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp.=35°C, [H$^+$]=0·05 mol dm^{-3}, [CAT]=2 x 10^{-3} mol dm^{-3},
μ=0·20 mol dm^{-3}, [CPC]=0·002 mol dm^{-3}

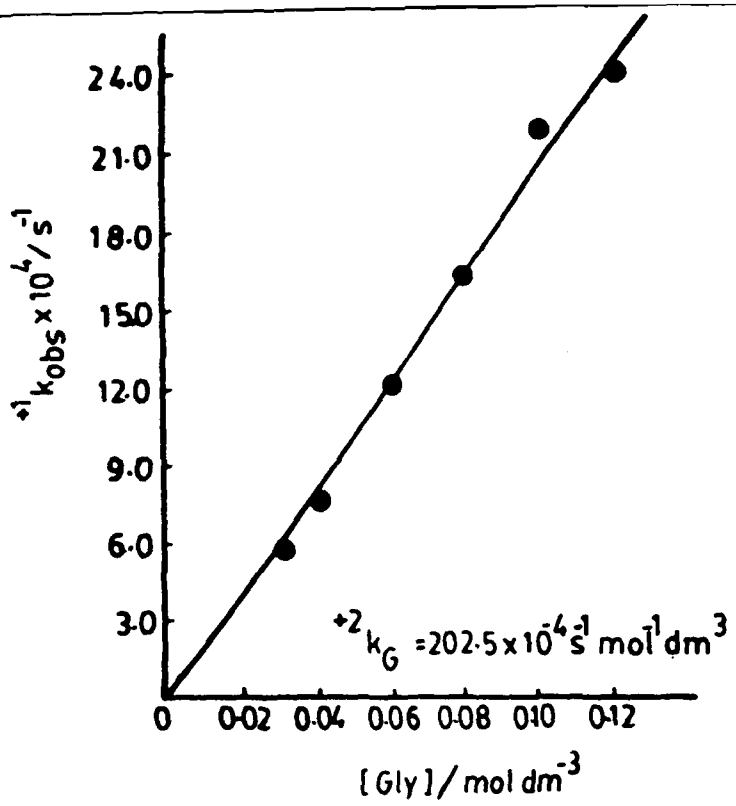


Figure 16b: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp = 35°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

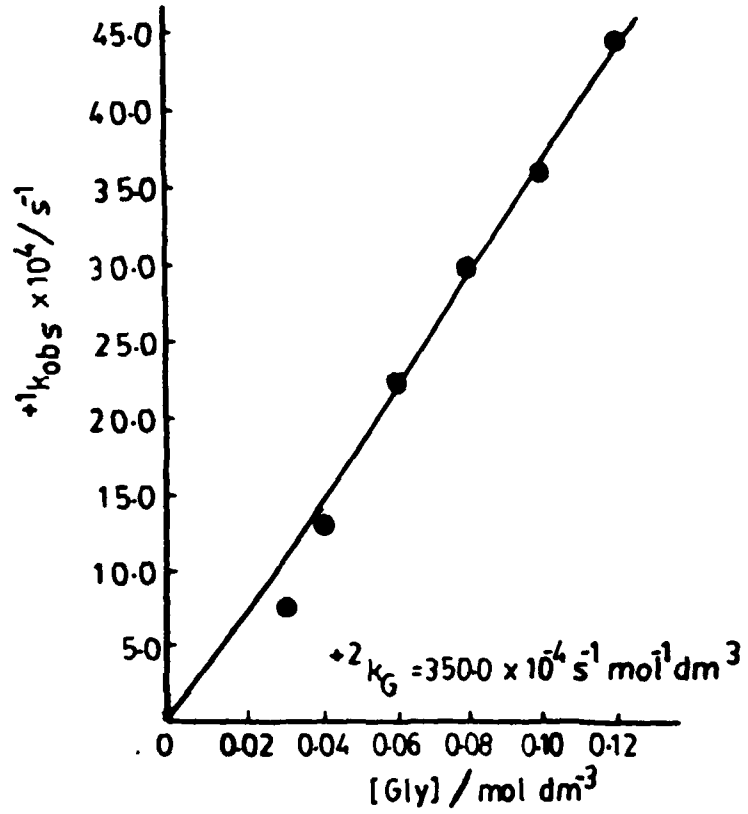


Figure 16c: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp = 35°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·006 mol dm^{-3}

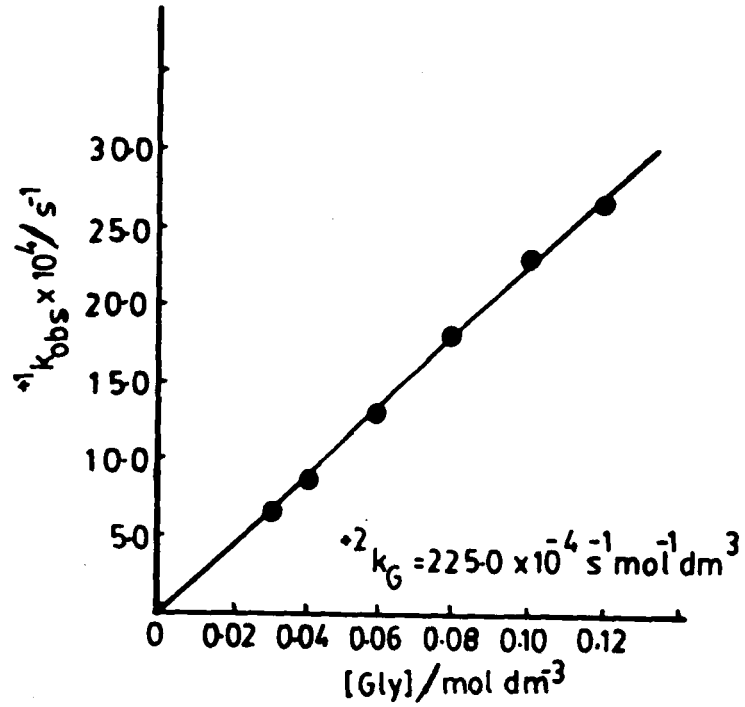


Figure 17a : Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp = 40°C, $[H^+]$ = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·002 mol dm^{-3}

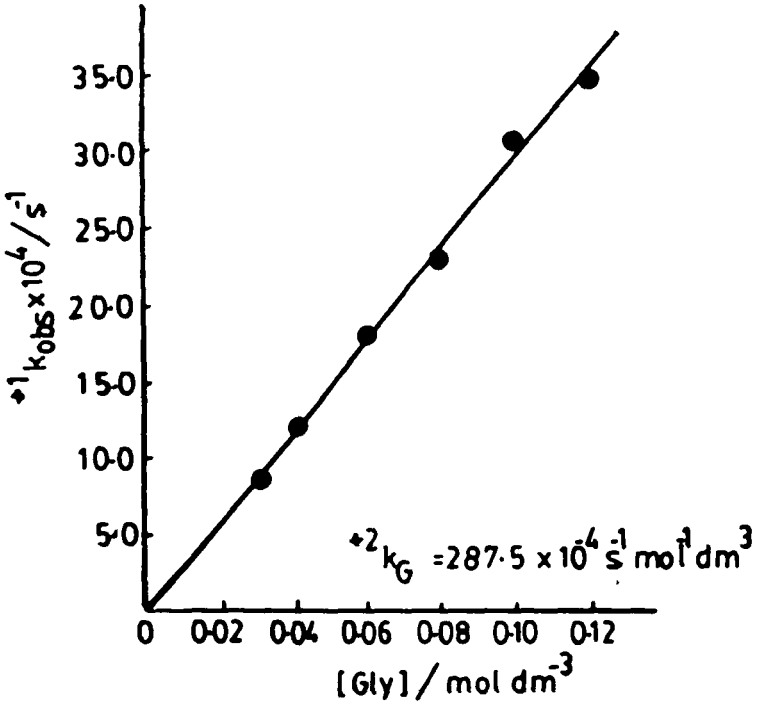


Figure 17b : Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp = 40°C, $[H^+]$ = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

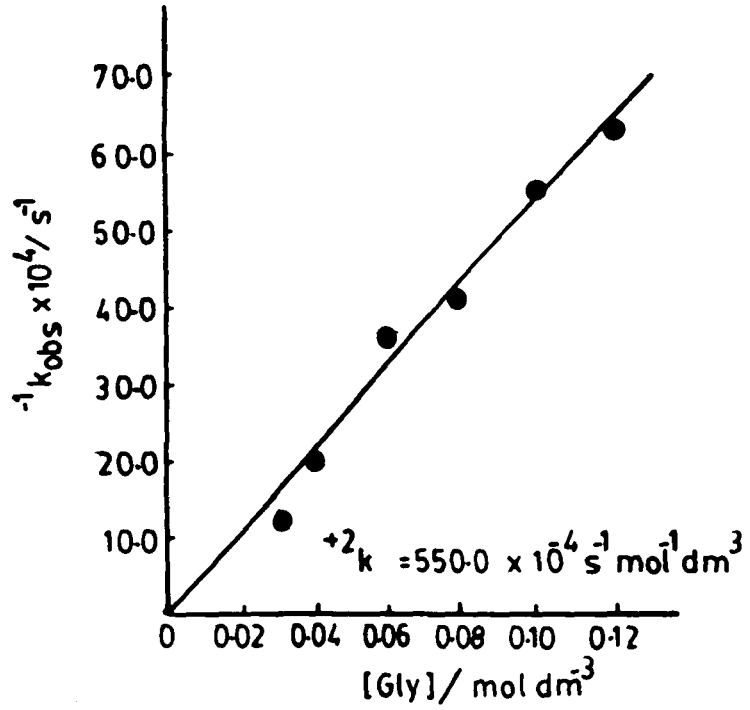


Figure 17c: Plot of $^{+1}k_{obs}$ VS [Gly] in the presence of CPC
Temp = 40°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·006 mol dm^{-3}

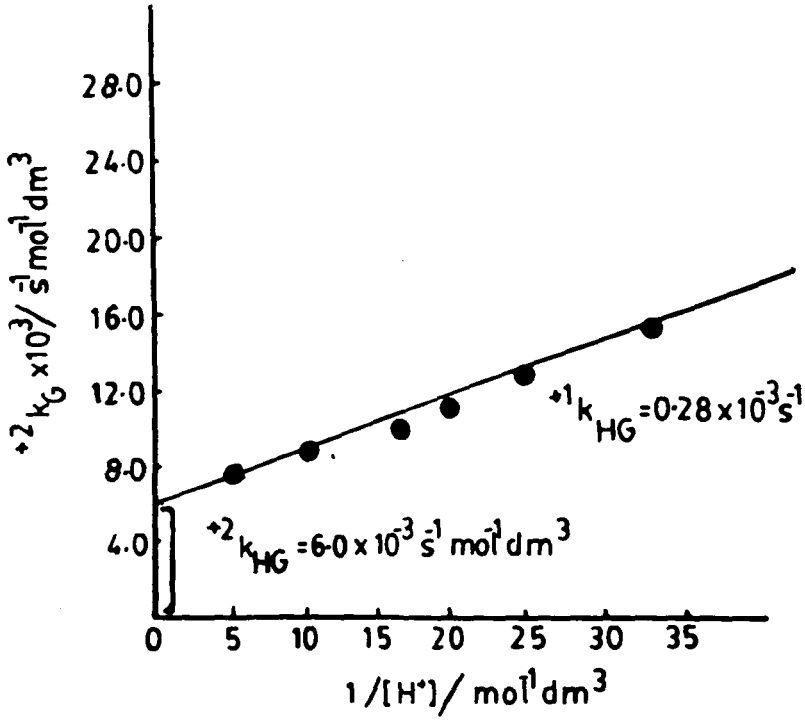


Figure 18a: Plot of $^{+2}k_G$ VS 1/[H$^+$] in the presence of CPC
Temp = 30°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0·20 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

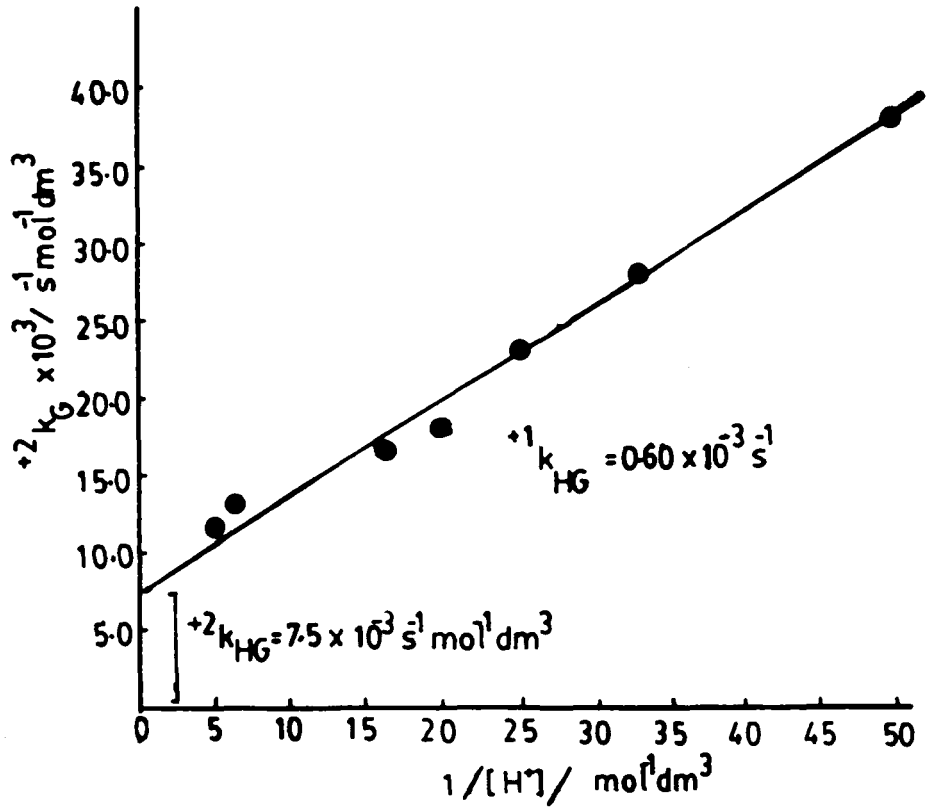


Figure 18b: Plot of $^{+2}k_G$ VS $1/[H^+]$ in the presence of CPC

Temp = 35°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

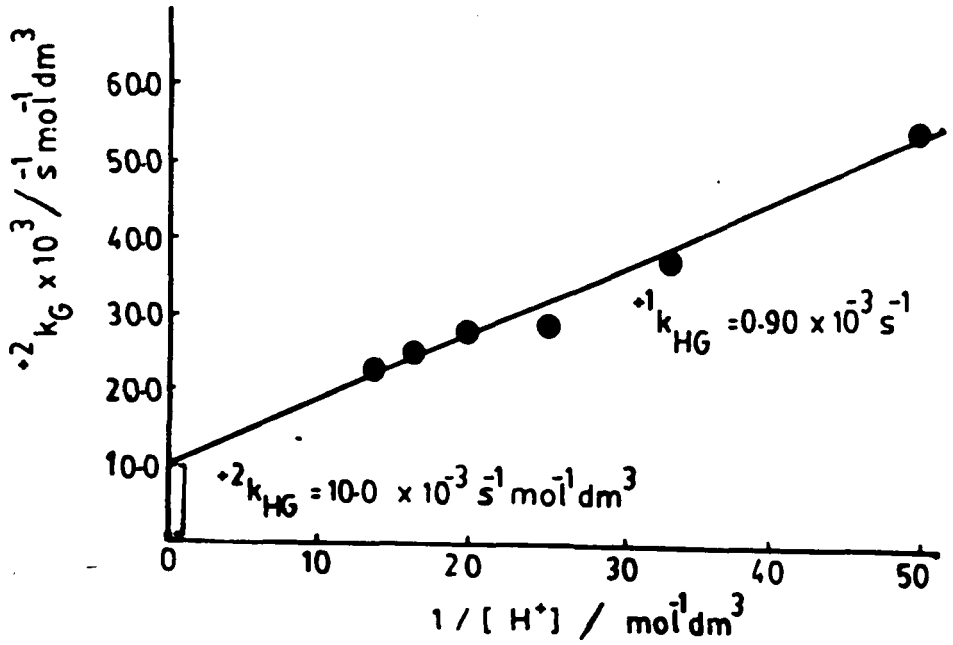


Figure 18c: Plot of $^{+2}k_G$ VS $1/[H^+]$ in the presence of CPC

Temp = 40°C, [Gly] = 0·03 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·20 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

Equation (22) has been verified from the linear plots between $^{+1}k_{obs}$ versus $[A]_0$ (vide Figs. 15 a,b,c to 17 a,b,c) at different conditions.

$$^{+2}k_G = \{^{+2}k_{HG} + {}^{+1}k_{HG} \cdot 1/[H^+]\} \qquad \text{----------} \quad (23)$$

where

$$^{+2}k_{HG} = \frac{k_1 K_A + k_4 K_O}{(K_A + K_O) + K_O K'_{OS}[D_0][S^{m+}]}$$

$^{+2}k_{HG}$ represents second order rate constant in the presence of CPC associated with reaction path is not affected by $[H^+]$.

and

$$^{+1}k_{HG} = \frac{k_2 K_A K_O + k'_5 K_A K_O K'_{OS}[D_0][S^{m+}]}{(K_A + K_O) + K_O K'_{OS}[D_0][S^{m+}]}$$

$^{+1}k_{HG}$ represents the first order rate constant in the presence of CPC associated with reaction path which is adversely affected by $[H^+]$.

The equation (23) stands varified as plots between $^{+2}k_G$ versus $1/[H^+]$are found to be linear at different temperatures (vide Figs. 18 a,b,c).

On keeping hydrogen ion concentration constant, the dependence of observed rate constant on CPC may be obtained as under

$$^{+2}k_G = \left\{\frac{(k_1 K_A + k_4 K_O)}{(K_A + K_O) + K_O K'_{OS}[D_0][S^{m+}]} + \frac{k_2 K_A K_O + k'_5 K_A K_O K'_{OS}[D_0][S^{m+}]}{(K_A + K_O) + K_O K'_{OS}[D_0][S^{m+}]} \cdot \frac{1}{[H^-]}\right\}$$

$$= \frac{k_1 K_A + k_2 K_A K_O/[H^+] + k_4 K_O}{(K_A + K_O) + K_O K'_{OS}[D_0][S^{m+}]} + \frac{k'_5 K_A K_O K'_{OS}[D_0][S^{m+}]/[H^+]}{(K_A + K_O) + K_O K'_{OS}[D_0][S^{m+}]}$$

$$^{+2}k_G = \left\{ \frac{\dfrac{k_1 K_A + k_2 K_A K_O/[H^+] + k_4 K_O}{(K_A + K_O)}}{1 + \dfrac{K_O K'_{OS}}{(K_A + K_O)}[D_0][S^{m+}]} + \frac{\dfrac{k'_5 K_A}{[H^-]} \dfrac{K_O K'_{OS}}{(K_A + K_O)}[D_0][S^{m+}]}{1 + \dfrac{K_O K'_{OS}}{(K_A + K_O)}[D_0][S^{m+}]} \right\}$$

$$^{+2}k_G = \left\{ \frac{^{02}k_G}{1 + K_- [D_0][S^{m+}]} + \frac{^{+2}k_{mG} K_+ [D_0][S^{m+}]}{1 + K_+ [D_0][S^{m+}]} \right\} \quad \text{---------- (24)}$$

where

$$^{02}k_G = \frac{k_1 K_A + k_2 K_A K_O/[H^+] + k_4 K_O}{(K_A + K_O)}$$

as obtained for reaction in the absence of surfactants.

$$^{-2}k_{mG} = \frac{k'_5 K_A}{[H^+]} \quad \text{and} \quad K_+ = \frac{K_O K'_{OS}}{(K_A + K_O)}$$

Substracting $^{02}k_G$ from both sides in equation (24).

$$^{+2}k_G - {}^{02}k_G = \frac{^{02}k_G}{1 + K_+ [D_0][S^{m+}]} + \frac{^{-2}k_{mG} K_+ [D_0][S^{m+}]}{1 + K_+ [D_0][S^{m+}]} - {}^{02}k_G$$

$$= \frac{^{02}k_G + {}^{+2}k_{mG} K_+ [D_0][S^{m+}] - {}^{02}k_G - {}^{02}k_G K_+ [D_0][S^{m+}]}{1 + K_+ [D_0][S^{m+}]}$$

$$^{+2}k_G - {}^{02}k_G = \frac{(^{+2}k_{mG} - {}^{02}k_G) K_+ [D_0][S^{m+}]}{1 + K_+ [D_0][S^{m+}]} \quad \text{---------- (25)}$$

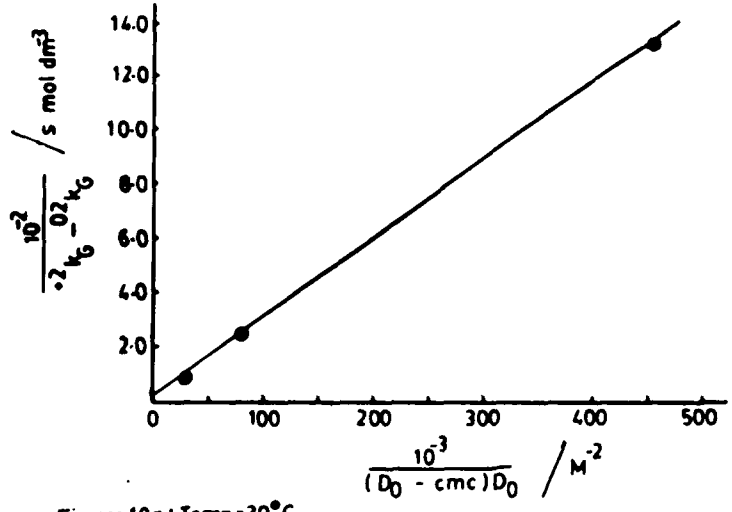


Figure 19a : Temp = 30°C

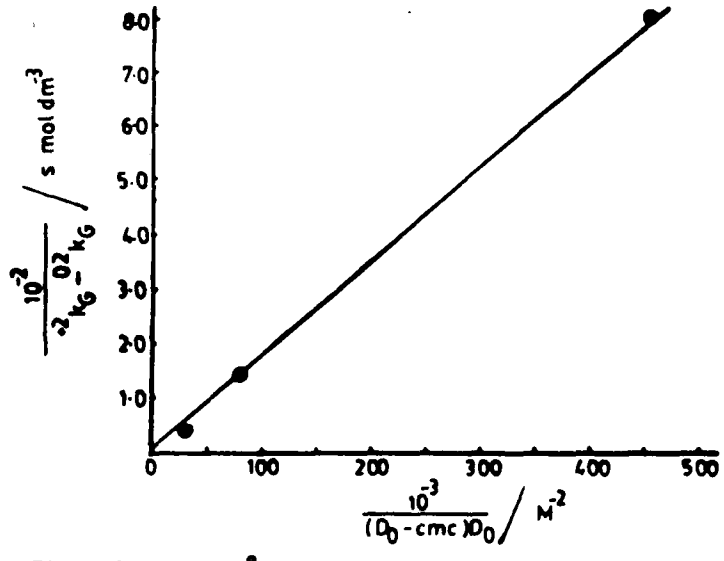


Figure 19b : Temp = 35°C

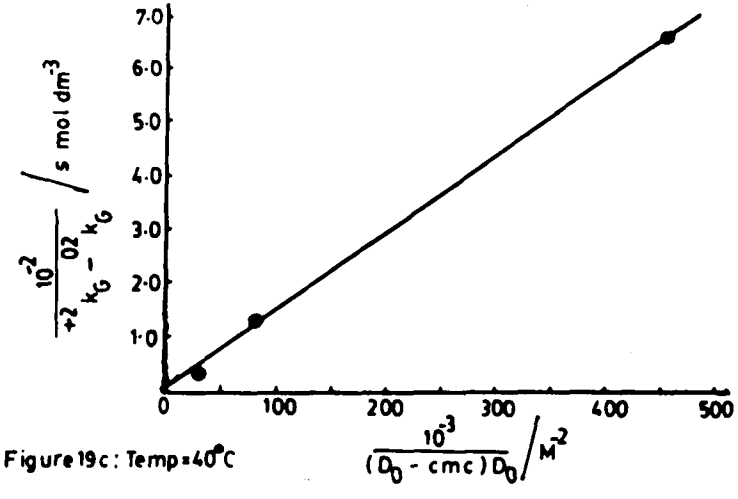


Figure 19c : Temp = 40°C

Figures 19 a,b,c ; Plots of $\frac{1}{\phi^2 k_G - 0^2 k_G}$ VS $\frac{1}{(D_0 - cmc)D_0}$ at different temperatures

TABLE-6 : Temperature dependence of $^{+2}k_{mG}$ and K_+ for glycine in the presence of CPC :

Temps. (°C)	$^{+2}k_{mG}$ x $10^3/s^{-1}$ mol^{-1} dm^3	$K_+/10^3$ $mol^{-1}dm^3$
30	108.25	0.6
35	113.00	1.1
40	121.00	1.3

Taking the reciprocal of equation (25), we get

$$\frac{1}{{}^{+2}k_G - {}^{02}k_G} = \frac{1}{{}^{+2}k_{mG} - {}^{02}k_G} + \frac{1}{{}^{+2}k_{mG} - {}^{02}k_G} \cdot \frac{1}{K_+ [D_0][S^{m+}]}$$

where

$$[S^{m+}] = \frac{D_0 - cmc}{N}$$

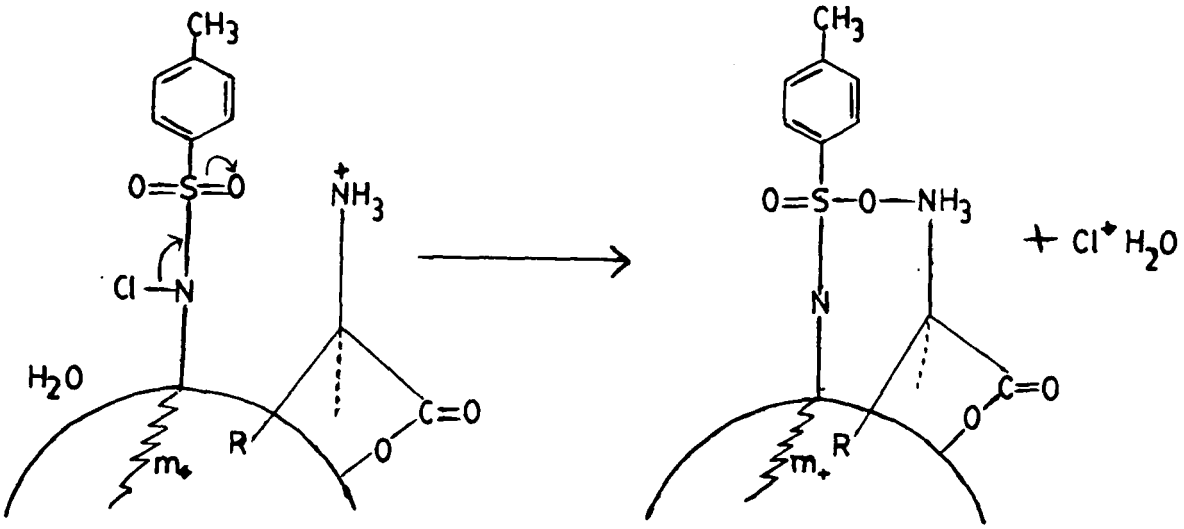
then

$$\frac{1}{{}^{+2}k_G - {}^{02}k_G} = \frac{1}{{}^{+2}k_{mG} - {}^{02}k_G} + \frac{1}{{}^{+2}k_{mG} - {}^{02}k_G} \cdot \frac{N}{K_+ (D_0 - cmc) D_0}$$

Where D_0 is the concentration of CPC used and N represents the aggregate number. The value of cmc for CPC has been taken as 9.0×10^{-4} which is only marginally affected by temperature change from 25° to 40°C[24]. The above equation has been tested by plots of $1/({}^{+2}k_G - {}^{02}k_G)$ versus $1/(D_0 - cmc) D_0$ which is found to be linear (vide Figs. 19 a,b,c) and the reciprocal of intercept of these plots gives $({}^{+2}k_{mG} - {}^{02}k_G)$ from which values of ${}^{+2}k_{mG}$ at different temperatures have been calculated alongwith its activation parametes and have also calculated and the K_+ calculated (Table 6). It may be pointed out again that K_+ does not represent simple binding parameter between oxidant and the micelles.

OXIDATIVE DEGRADATION OF ALANINE IN THE PRESENCE OF CPC :

In the case of alanine it has been observed that plots between $^{-1}k_{obs}$ versus [alanine] give a small positive intercept, it may be recalled that in case of glycine these plots were passing through origin. The above observation may be accommodated by marginal modification of the scheme proposed for glycine.It is to be noted further that this difference is not observed in the absence of surfactant and also when reaction is carried out in the presence of SDS. It is, therefore, suggested that CPC-oxidant complex, $(OXDS)^m$, is interacting with water catalyzed by the presence of alanine. This may be shown by the following reaction model.



fast

$$Cl^+ H_2O \longrightarrow HCl + H^+ + 1/2\ O_2$$

In view of the above, a reaction path for the oxidation of water has to be included as shown in step (10).

Reaction Mechamism and Rate Law :

$$AH^+ \overset{K_A}{\rightleftharpoons} A + H^+ \quad \text{---------- (1)} \quad K_A/[H^+] = [A]/[AH^+]$$

$$OXH \overset{K_O}{\rightleftharpoons} O\bar{X} + H^+ \quad \text{---------- (2)} \quad K_O/[H^+] = [O\bar{X}]/[OXH]$$

$$OXD \overset{K_d}{\rightleftharpoons} O\bar{X} + D^+ \quad \text{---------- (3)} \quad K_d/[D^+] = [O\bar{X}]/[OXD]$$

$$OXD + S^{m+} \overset{K_{OS}}{\rightleftharpoons} [OXDS]^{m+} \quad \text{------ (4)} \quad K_{OS} = [OXDS]^{m+}/[OXD][S^{m+}]$$

Where $[D^-] = [D_0] - [S^{m+}]$, as shown earlier in case of glycine in the presence of CPC.

$$A + OXH \xrightarrow{k_1} \cdots\cdots \quad \text{----------} \quad (5)$$

$$A + O\bar{X} \xrightarrow{k_2} \cdots\cdots \quad \text{----------} \quad (6)$$

$$OXH + AH^- \xrightarrow{k_3} \cdots\cdots \quad \text{----------} \quad (7)$$

$$O\bar{X} + AH^+ \xrightarrow{k_4} \cdots\cdots \quad \text{----------} \quad (8)$$

$$A + (OXDS)^{m+} \xrightarrow{k'_5} \cdots\cdots \quad \text{----------} \quad (9)$$

$$(OXDS)^{m+} + H_2O \xrightarrow{k'_{H_2O}} \cdots\cdots \quad \text{----------} \quad (10)$$

Using the mass balanced equation for amino acid concentration

$$[A]_0 = [A] + [AH^+]$$

$$[A]_0 = \frac{[A]}{K_A}(K_A + [H^+]) \qquad \text{----------} \quad (11)$$

$$= \frac{[AH^+]}{[H^+]}(K_A + [H^+]) \qquad \text{----------} \quad (12)$$

where,

$$D = (K_A + [H^+])$$

Using mass balanced equation for oxidant concentration

$$[OX]_T = [\overline{OX}]+[OXH]+[OXD]+[OXDS]^{m+}$$

$$= [\overline{OX}]\,(1+[H^+]/K_O + [D^+]/K_d + K_{OS}\,[S^{m+}]\,[D^+]/K_d])$$

$$= \frac{[\overline{OX}]}{K_O K_d}(K_O K_d+K_d[H^+]+K_O[D^+]+K_O K_{OS}\,[D^+][S^{m+}]) \text{ ----- } (13)$$

$$= \frac{[OXH]}{K_d[H^+]}(K_O K_d+K_d[H^+]+K_O[D^-]+K_O K_{OS}\,[D^+][S^{m+}]) \text{ ----- } (14)$$

$$= \frac{[OXDS]^{m+}}{K_O K_{OS}[D^+][S^{m+}]}(K_O K_d+K_d[H^+]+K_O[D^+]+K_O K_{OS}\,[D^+][S^{m+}])$$

$$\text{--------} \quad (15)$$

where

$$D'' = (K_O K_d+K_d[H^+]+K_O[D^+]+K_O K_{OS}\,[D^+][S^{m+}]) \qquad \text{-----} \quad (16)$$

simplifying

$$DD'' = (K_A+[H^+])\,(K_O K_d+K_d[H^+]+K_O[D^+]+K_O K_{OS}\,[D^+][S^{m+}]) \text{ ----- } (17)$$

putting the value $[D^+] = [D_0] - [S^{m+}]$ in above equation

$$DD'' = K_A (K_d K_O + K_O [D_0 - S^{m+}] + K_O K_{OS} [D_0 - S^{m+}] [S^{m+}])$$

$$+(K_A K_d + K_d K_O + K_O[D_0 - S^{m+}] + K_O K_{OS}[D_0 - S^{m+}][S^{m+}]) [H^+] + ...$$

neglecting $[H^+]^2$ and $[S^{m+}]^2$ and assuming $K_A < 1$ and $K_O < 1$.

$$DD'' \approx (K_A K_d + K_d K_O + K_O K_{OS} [D_0] [S^{m+}]) [H^+] \qquad \text{--------- (18)}$$

$$= D'_S [H^+]$$

where,

$$D'_S = (K_A K_d + K_d K_O + K_O K_{OS} [D_0] [S^{m+}]) \qquad \text{--------- (19)}$$

The rate expression may be obtained as below :

$$\text{reaction rate} = (k_1 [OXH] + k_2 [\overline{OX}] + k'_5 [OXDS]^{m+}) [A]$$

$$+ (k_3[OXH] + k_4[\overline{OX}]) [AH^+] + K'_{H_2O} [OXDS]^{m+}$$

$$= (k_1 K_d [H^+] + k_2 K_O K_d + k'_5 K_O K_{OS} [D_0][S^{m+}]) \; K_A \frac{[A]_0[OX]_T}{D'_S [H^+]}$$

$$+ (k_3 K_d [H^+] + k_4 K_O K_d) \frac{[A]_0[OX]_T [H^+]}{D'_S [H^+]} + \frac{K'_{H_2O} K_O K_{OS}[D_0][S^{m+}][OX]_T}{D''}$$

$$= (k_1 K_A K_d + k_2 K_A K_O K_d/[H^+] + k'_5 K_A K_O K_{OS} [D_0][S^{m+}]/[H^+]$$

$$+ k_3 K_d [H^+] + k_4 K_O K_d) \frac{[A]_0[OX]_T}{D'_S [H^+]} + \frac{K'_{H_2O} K_O K_{OS}[D_0][S^{m+}][OX]_T}{D''}$$

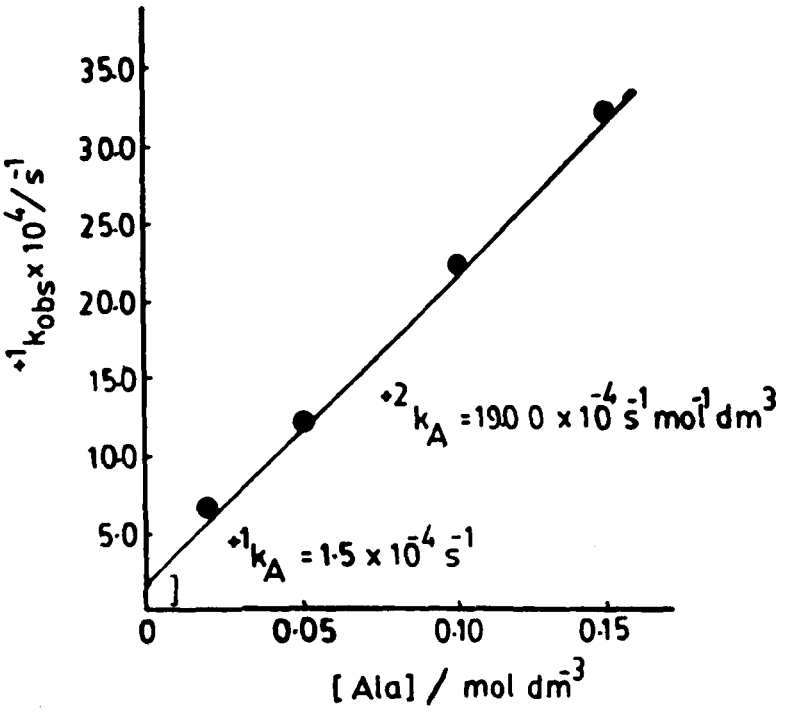


Figure 20a: Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC
Temp = 30°C, $[H^+]$=0.05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0.15 mol dm^{-3}, [CPC] = 0.002 mol dm^{-3}

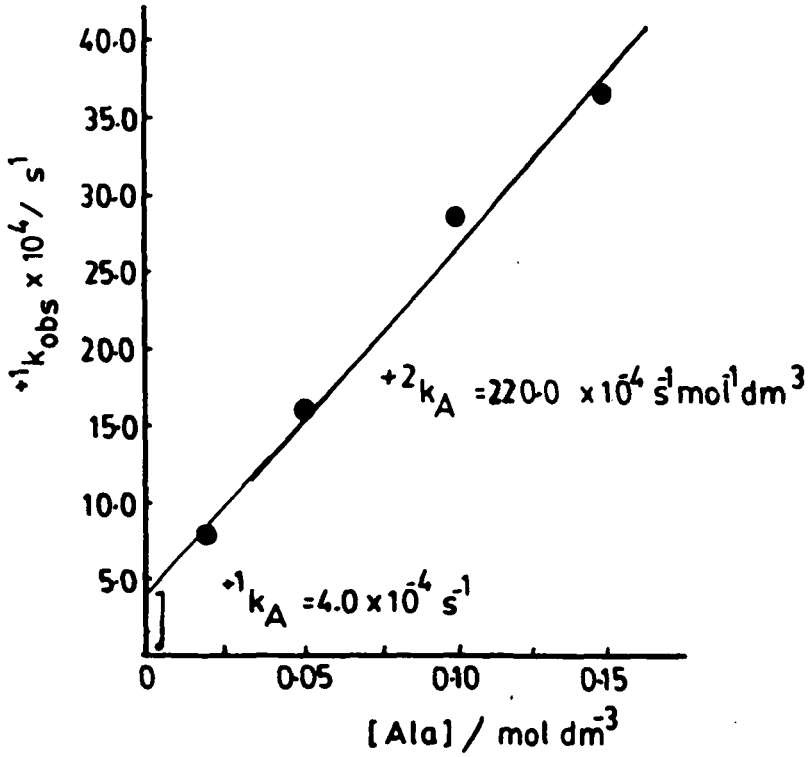


Figure 20b: Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC
Temp = 30°C, $[H^+]$=0.05 mol dm^3, [CAT] = 2×10^{-3} mol dm^{-3},
μ = 0.15 mol dm^3, [CPC] = 0.003 mol dm^3

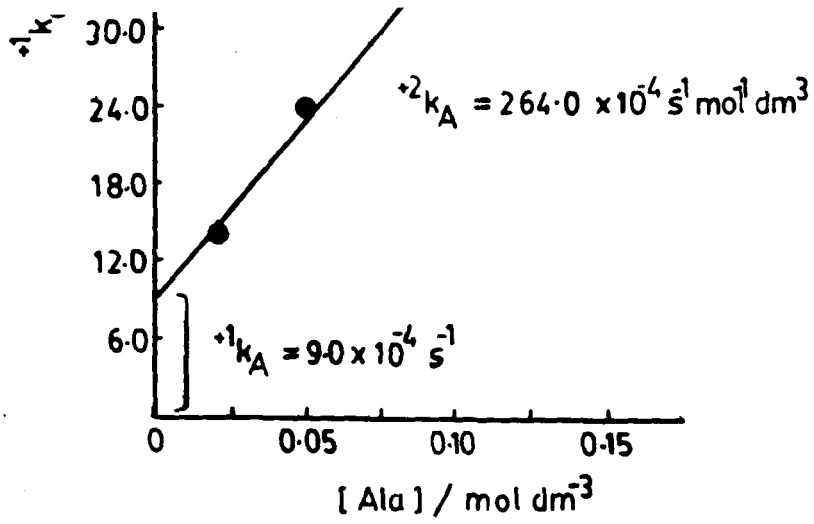


Figure 20c: Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC
Temp=30°C, [H$^+$]=0·05 mol dm^{-3}, [CAT]=2 x 10^{-3} mol dm^{-3},
μ = 0·15 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

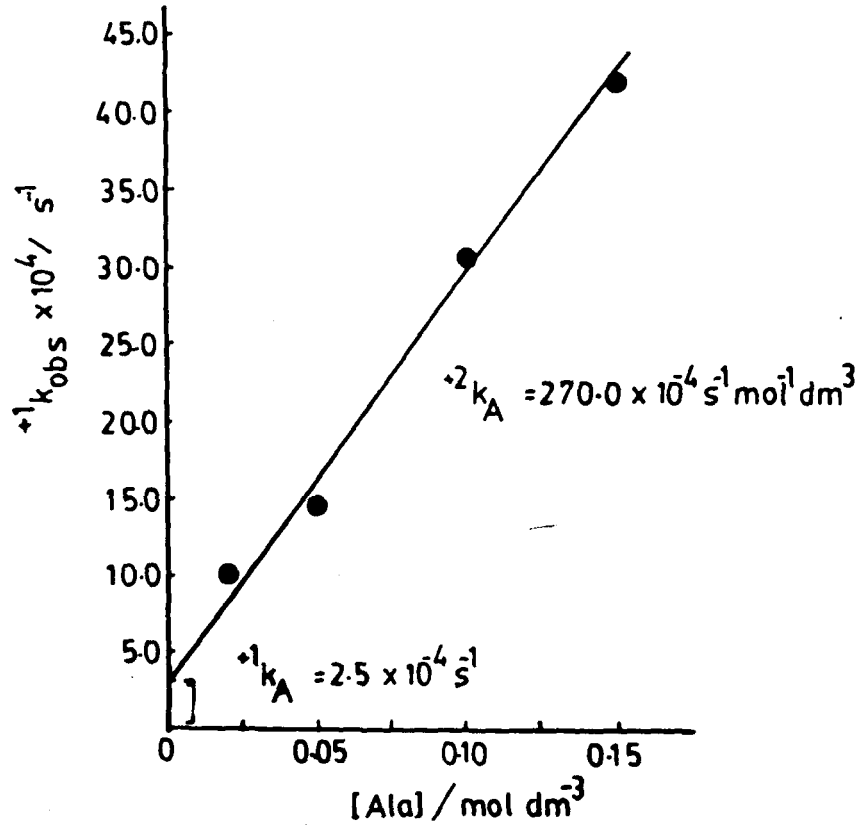


Figure 21a : Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC
Temp = 35°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2 x 10^{-3} mol dm^{-3},
μ = 0·15 mol dm^{-3}, [CPC] = 0·002 mol dm^{-3}

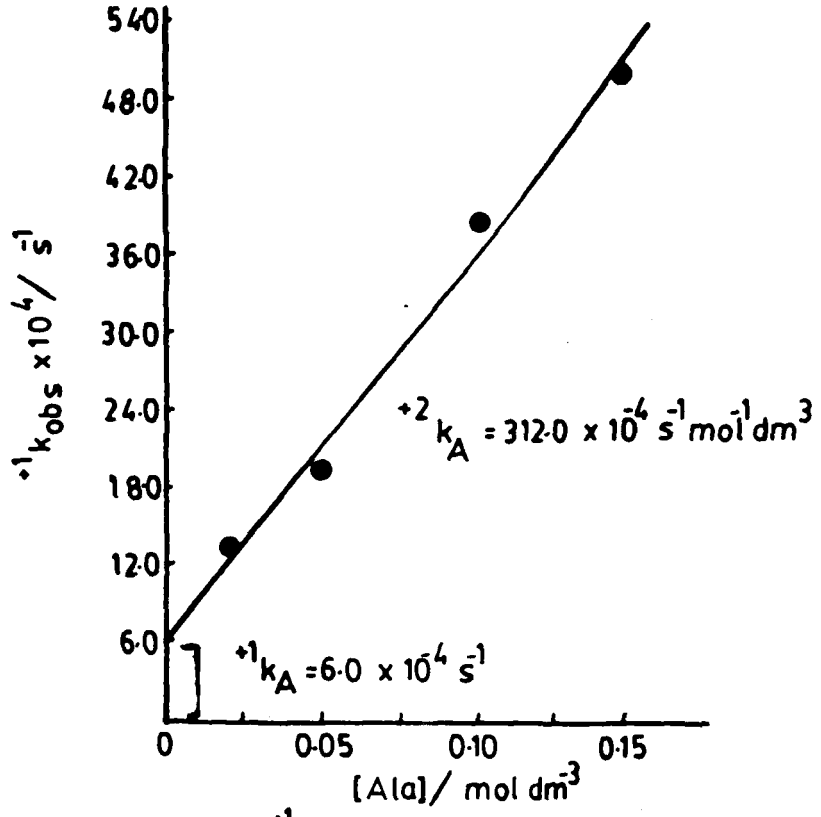


Figure 21b : Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC

Temp = 35° C, $[H^+]$ = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [CPC] = 0·003 mol dm^{-3}

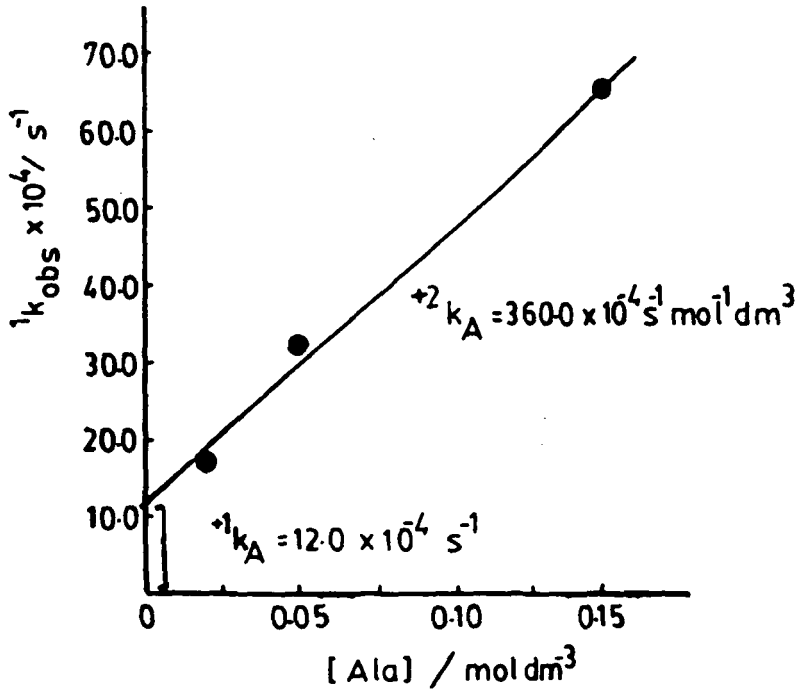


Figure 21c : Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC

Temp = 35° C, $[H^+]$ = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [CPC] = 0·004 mol dm^{-3}

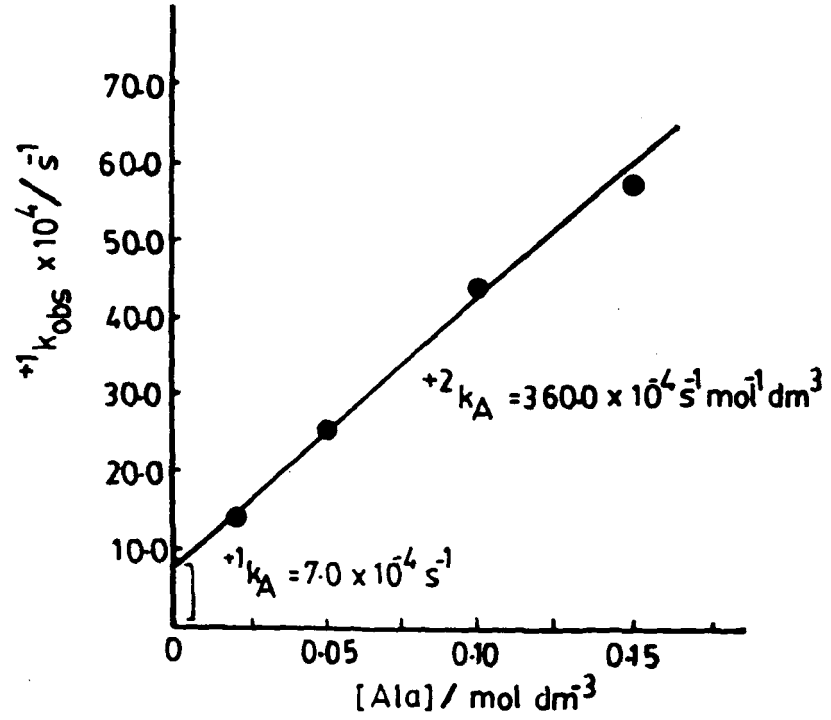


Figure22 a: Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC

Temp = 40°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [CPC] = 0·002 mol dm^{-3}

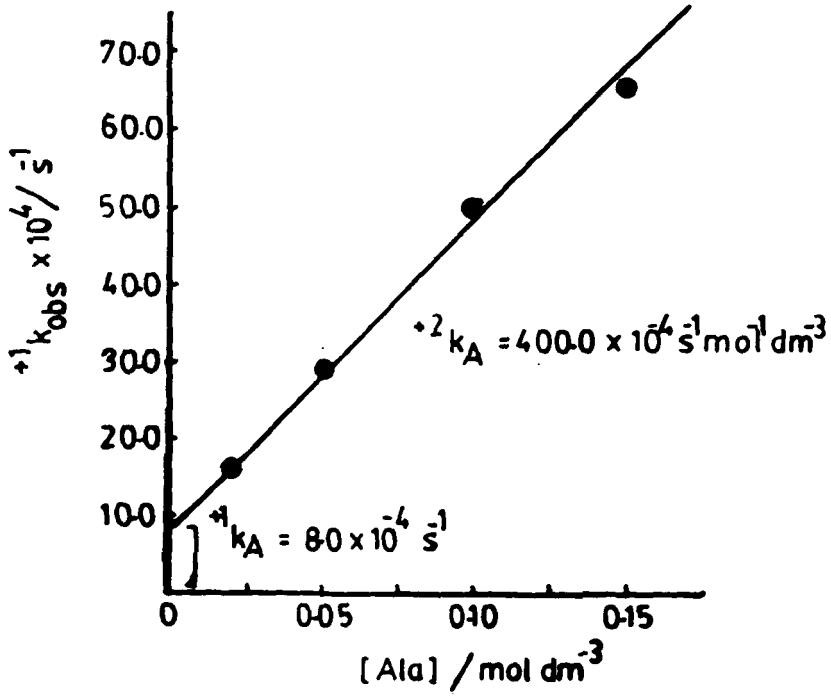


Figure22b: Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC

Temp = 40°C, [H$^+$] = 0·05 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3},

μ = 0·15 mol dm^{-3}, [CPC] = 0·003 mol dm^{-3}

Assuming $k_3 << 1$

reaction rate

$$= [\{k_1K_AK_d + k_4K_OK_d + \frac{k_2K_AK_OK_d + k'_5K_AK_OK_{OS}[D_0][S^{m+}]}{[H^+]}\} \frac{[A]_0\,[OX]_T}{D'_S} + k_S[ox]_T$$

$$= ({}^{+2}k_A\,[A]_0 + k_s)\,[OX]_T = {}^{+1}k_{obs}\,[OX]_T$$

when

$${}^{+1}k_{obs} = {}^{+2}k_A\,[A]_0 + k_S \qquad \text{----------} \qquad (20)$$

where

$$k_S = \frac{k'_{H_2O}K_OK_{OS}\,[D_0][S^{m+}]}{D''}$$

and

$${}^{+2}k_A = \frac{(k_1K_A + k_4K_O)\,K_d}{(K_A + K_O + K_OK'_{OS}\,[D_0]\,[S^{m+}])K_d}$$

$$+ \frac{(k_2K_AK_O + k'_5K_AK_OK'_{OS}[D_0][S^{m+}])K_d}{(K_A + K_O + K_OK'_{OS}\,[D_0]\,[S^{m+}])K_d} \cdot \frac{1}{[H^+]}$$

and

$$K'_{OS} = \frac{K_{OS}}{K_d}$$

equation (20) has been verified from the linear plots between ${}^{+1}k_{obs}$ versus $[A]_0$ which k_S as intercept and the second order rate constant, ${}^{+2}k_A$, is given by the slopes under different conditions (vide Figs. 20 a,b,c to 22 a,b,c).

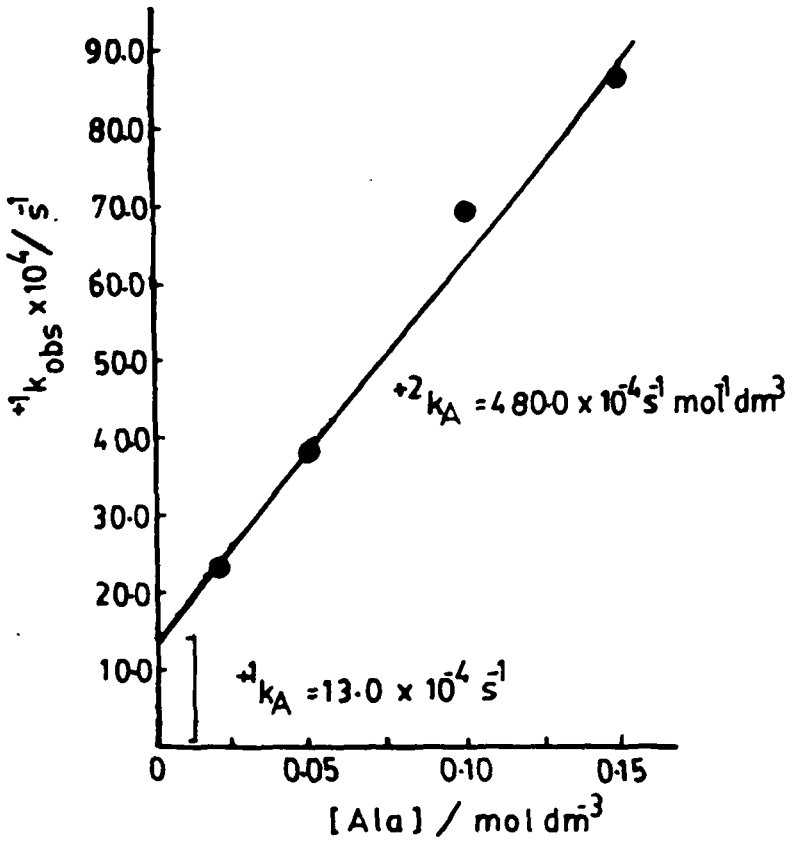


Figure 22c: Plot of $^{+1}k_{obs}$ VS [Ala] in the presence of CPC

Temp.=40°C, $[H^+]$=0.05 mol dm^{-3}, [CAT]=2x10^{-3} mol dm^{-3},

μ=0.15 mol dm^3, [CPC]=0.004 mol dm^3

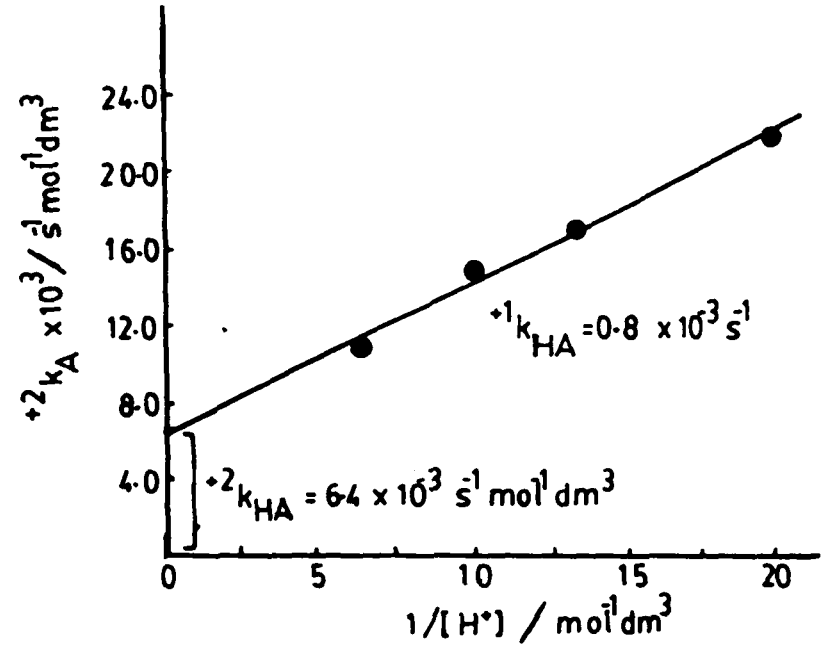


Figure 23a: Plot of $^{+2}k_A$ VS 1/[H$^+$] in the presence of CPC

Temp = 30°C, [Ala]= 0.15 mol dm^{-3}, [CAT]=2x10^{-3} mol dm^{-3},

μ=0.15 mol dm^{-3}, [CPC]=0.002 mol dm^{-3}

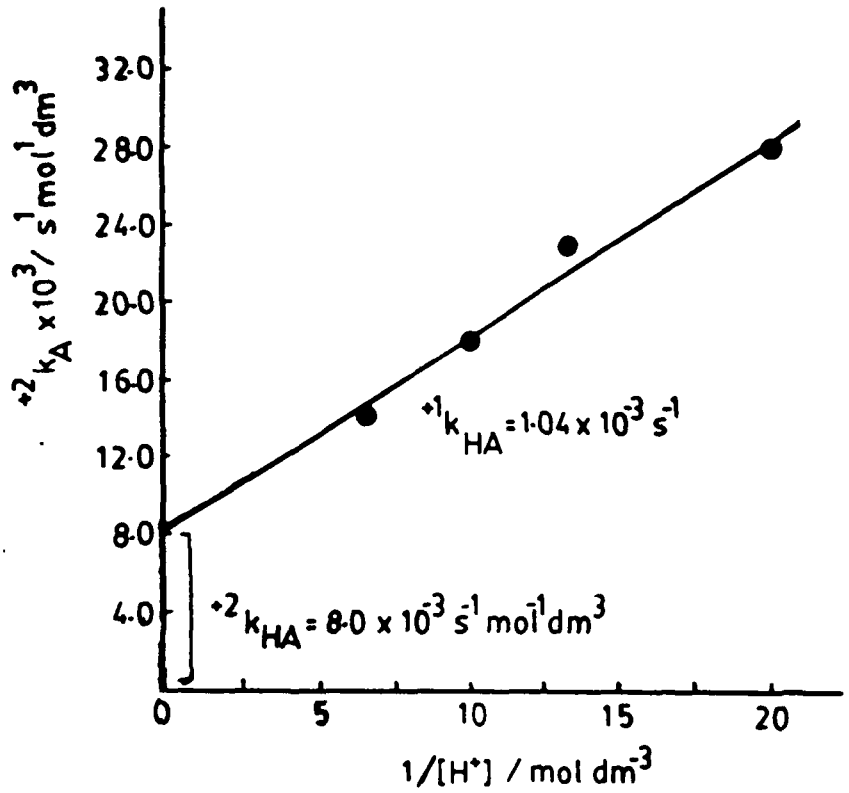


Figure 23b: Plot of $^{+2}k_A$ VS $1/[H^+]$ in the presence of CPC

Temp = 35°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3}, μ = 0·15 mol dm^{-3}, [CPC] = 0·002 mol dm^{-3}

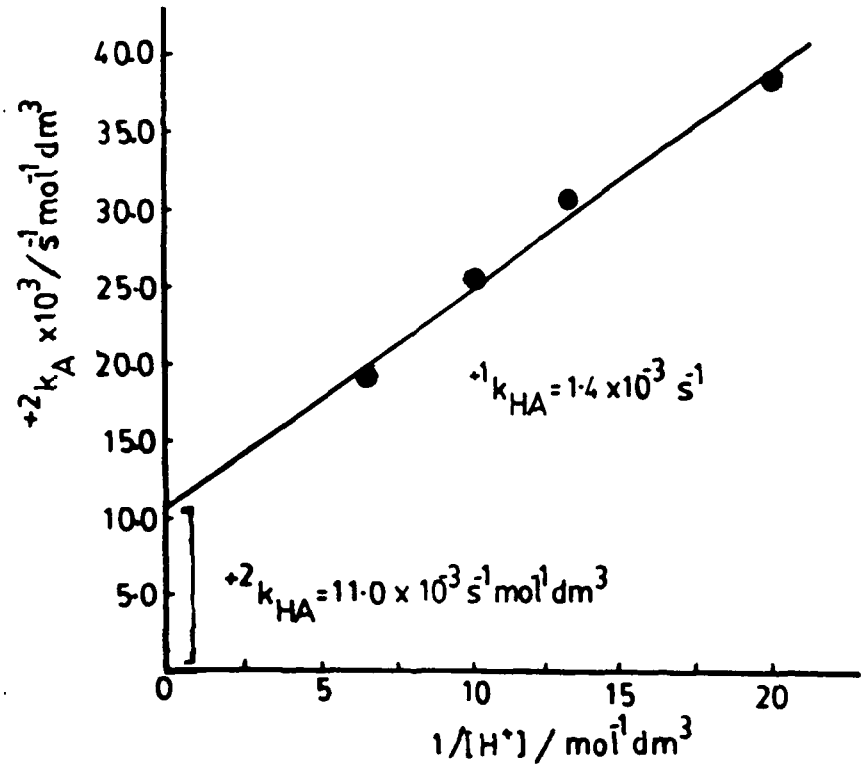


Figure 23c: Plot of $^{+2}k_A$ VS [Ala] in the presence of CPC

Temp = 40°C, [Ala] = 0·15 mol dm^{-3}, [CAT] = 2×10^{-3} mol dm^{-3}, μ = 0·15 mol dm^{-3}, [CPC] = 0·002 mol dm^{-3}

At constant CPC :

The dependence of reaction rate on hydrogen ion concentration has been studied at constant CPC and other kinetic parameters. The equation (20) may be rearranged to show the dependence of $^{+2}k_A$ on $[H^+]$ as below :

$$\text{reaction rate} = [\{^{+2}k_{HA} + {}^{+1}k_{HA} \cdot \frac{1}{[H^+]}\} [A]_0 + k_S] [OX]_T$$

$$= {}^{+2}k_A [A]_0 [OX]_T + k_S [OX]_T$$

$$^{+2}k_A = \{^{2}k_{HA} + {}^{+1}k_{HA} \cdot \frac{1}{[H^+]}\} \text{ ---------- } (21)$$

where

$$^{+2}k_{HA} = \frac{(k_1K_A + k_4K_O)}{(K_A + K_O) + K_OK'_{OS}[D_0][S^{m+}]}$$

and

$$^{+1}k_{HA} = \frac{k_2K_AK_O + k'_5K_AK_OK'_{OS}[D_0][S^{m+}]}{(K_A + K_O) + K_OK'_{OS}[D_0][S^{m+}]}$$

The equation (21) is verified as plots between $^{+2}k_A$ versus $1/[H^+]$ are found to be linear at different temperatures (vide Figs. 23 a,b,c). The intercepts of these plots give $^{+2}k_{HA}$ and the slopes, $^{+1}k_{HA}$.

At constant hydrogen ion concentration :

The dependence of ${}^{+2}k_A$ on CPC concentration at constant hydrogen ion concentration and other parameters may be obtained by rearranging equation (21).

$$ {}^{+2}k_A = \{ {}^{2}k_{HA} + {}^{+1}k_{HA} \cdot \frac{1}{[H^+]} \} \text{ ---------- } (21) $$

$$ {}^{+2}k_A = \{ \frac{(k_1K_A + k_4K_O)}{(K_A + K_O) + K_OK_{OS}[D_0][S^{m+}]} + \frac{k_2K_AK_O + k_5K_AK_OK'_{OS}[D_0][S^{m+}]}{(K_A + K_O) + K_OK'_{OS}[D_0][S^{m+}]} \cdot \frac{1}{[H^+]} \} $$

$$ {}^{+2}k_A = \frac{k_1K_A + k_2K_AK_O/[H^+] + k_4K_O}{(K_A + K_O) + K_OK'_{OS}[D_0][S^{m+}]} + \frac{k'_5K_AK_OK'_{OS}[D_0][S^{m+}]/[H^-]}{(K_A + K_O) + K_OK'_{OS}[D_0][S^{m+}]} $$

$$ {}^{+2}k_A = \frac{(k_1K_A + k_2K_AK_O/[H^-] + k_4K_O)\ \frac{1}{K_A + K_O}}{1 + \frac{K_OK'_{OS}}{K_A + K_O} \cdot [D_0][S^{m+}]} + \frac{\frac{k'_5K_A}{[H+]} \cdot \frac{K_OK'_{OS}}{K_A + K_O} \cdot [D_0][S^{m+}]}{1 + \frac{K_OK'_{OS}}{K_A + K_O} \cdot [D_0][S^{m+}]} $$

$$^{+2}k_A = \frac{^{02}k_A}{1 + K_+ [D_0] [S^{m}\ ]} + \frac{^{+2}k_{mA}\, K_+ [D_0] [S^{m+}]}{1 + K_+ [D_0] [S^{m+}]} \qquad \text{------- (22)}$$

where $^{+2}k_{mA}$ signifying second order rate constant in the micellar phases of CPC is given as,

$$^{+2}k_{mA} = \frac{k'_5 K_A}{[H^+]} \qquad \text{and} \qquad K_+ = \frac{K_O K'_{OS}}{K_A + K_O}$$

Subracting $^{02}k_A$ both side in equation (22)

$$^{+2}k_A - {}^{02}k_A = \frac{^{02}k_A}{1 + K_+ [D_0] [S^{m+}]} + \frac{^{+2}k_{mA}\, K_+ [D_0] [S^{m+}]}{1 + K_+ [D_0] [S^{m+}]} - {}^{02}k_A$$

$$= \frac{^{02}k_A + {}^{+2}k_{mA}\, K_+ [D_0] [S^{m+}] - {}^{02}k_A - {}^{02}k_A\, K_+ [D_0] [S^{m+}]}{1 + K_+ [D_0] [S^{m+}]}$$

$$^{+2}k_A - {}^{02}k_A = \frac{(^{+2}k_{mA} - {}^{02}k_A)\, K_+ [D_0] [S^{m+}]}{1 + K_+ [D_0] [S^{m+}]}$$

Taking the reciprocal of the above equation, we get,

$$\frac{1}{^{+2}k_A - {}^{02}k_A} = \frac{1}{^{+2}k_{mA} - {}^{02}k_A} + \frac{1}{^{+2}k_{mA} - {}^{02}k_A} \cdot \frac{1}{K_+ [D_0] [S^{m+}]} \qquad \text{---- (23)}$$

we know that

$$[S^{m+}] = \frac{D_0 - cmc}{N}$$

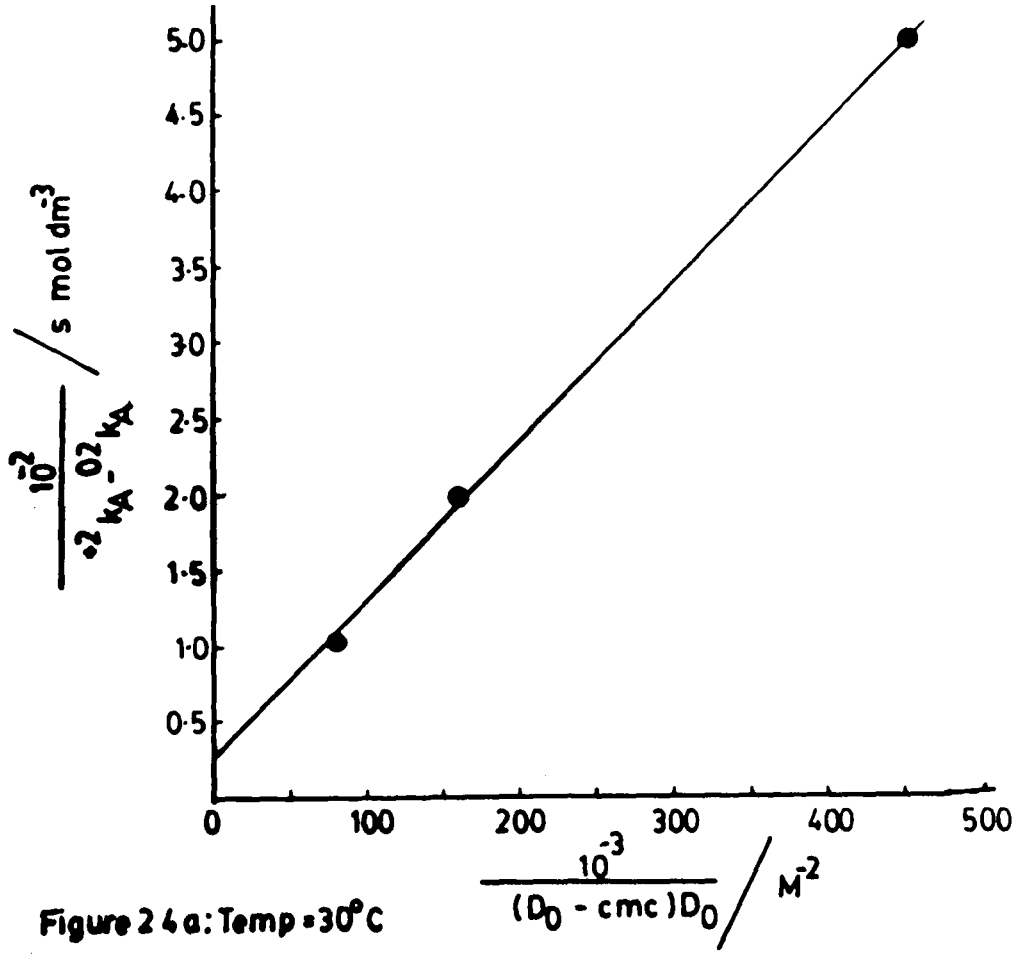


Figure 24 a: Temp =30°C

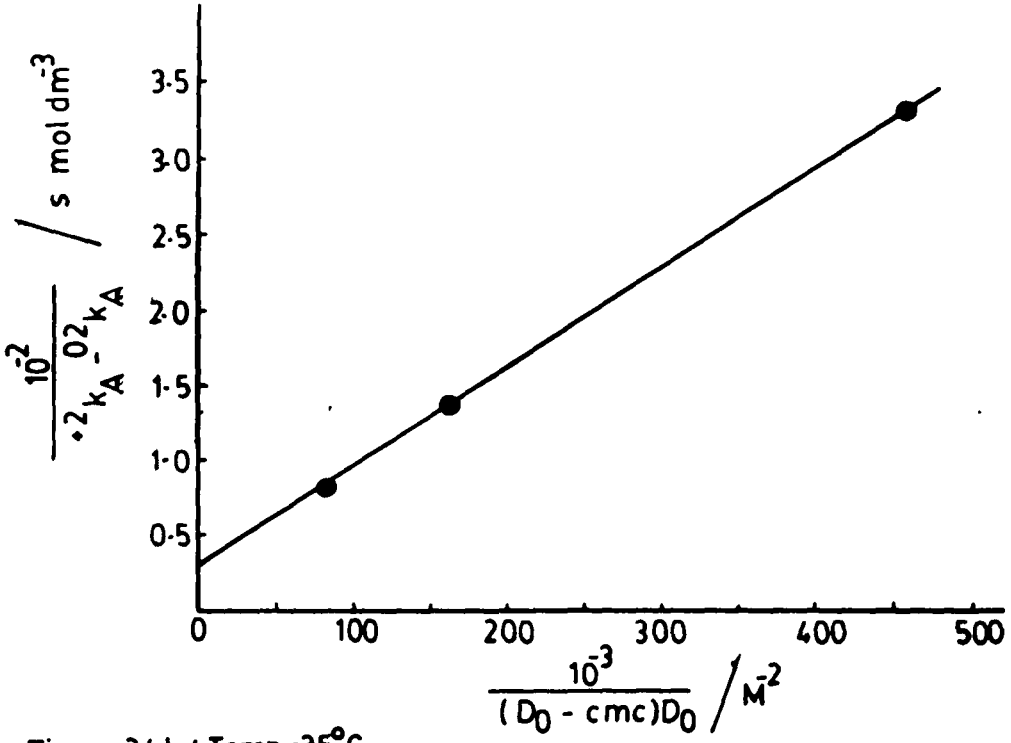


Figure 24 b : Temp =35°C

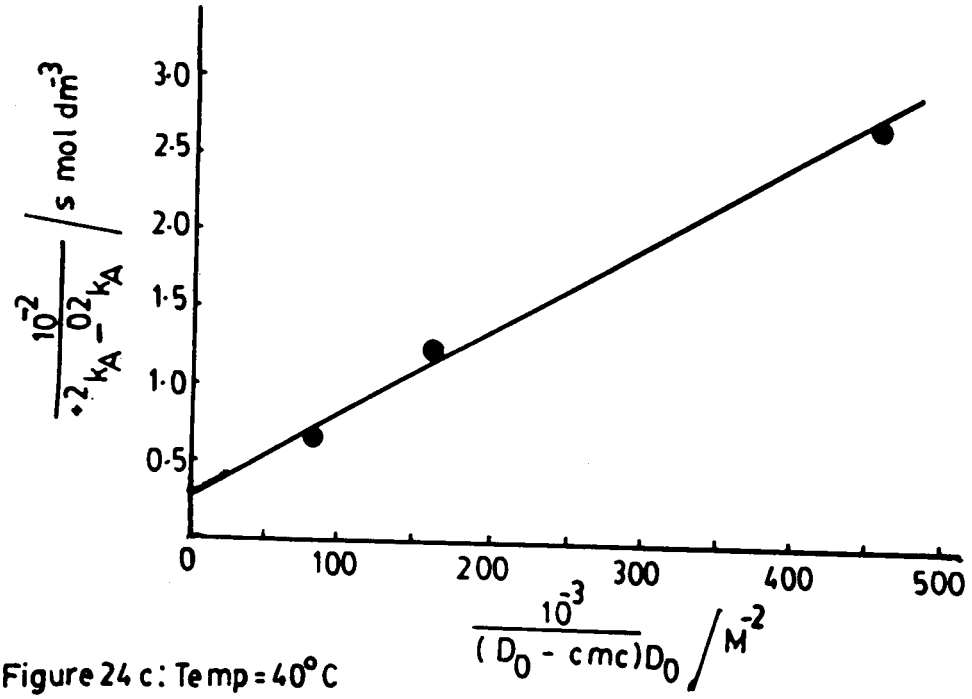


Figure 24 c: Temp = 40°C

Figures 24 a,b,c : Plots of $\frac{1}{\phi^2 k_A - \phi^2 k_A}$ VS $\frac{1}{(D_0 - cmc)D_0}$ at different temperatures

TABLE-7 : Temperature dependence of $^{+2}k_{mA}$ and K_{+} for alanine in the presence of CPC :

Temps. (°C)	$^{+2}k_{mA}$ x $10^3/s^{-1}$ mol^{-1} dm^3	$K_{+}/10^3$ $mol^{-1}dm^3$
30	57.0	2.3
35	64.0	3.6
40	72.4	4.3

Putting the value of [S^{m+}] in equation (23).

$$\frac{1}{{}^{+2}k_A - {}^{02}k_A} = \frac{1}{{}^{+2}k_{mA} - {}^{02}k_A} + \frac{1}{{}^{+2}k_{mA} - {}^{02}k_A} \cdot \frac{N}{K_+ (D_0 - cmc)\, D_0}$$

Where D_0 is the concentration of CPC used and N represents the aggregate number. The value of cmc for CPC has been used as 9.0×10^{-4} [24]. The above equation has been tested by plots of $1/{}^{+2}k_A - {}^{02}k_A$ versus $1/(D_0\text{-cmc})\, D_0$ which is found to be linear (vide Figs. 24 a,b,c) and value of ${}^{+2}k_{mA}$ and K_+ at different temperatures have been evaluated (Table 7).

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COMPARATIVE STUDY OF ACTIVATION PARAMETERS

Activation parameters in the absence of surfactants :

Comparing the activation parameters it is noted that the activation energy of glycine is much higher in comparison to the activation energy of alanine. Further, it is observed that in both the cases the activation energy associated with reaction path unaffected by hydrogen ion is much greater than the activation energies associated with the reaction path adversely affected by hydrogen ion (Table 1 and 2). The pre-exponential factor is lower for alanine in comparison to pre-exponential factor for glycine. In view of complex nature of $^{01}k_H$ and $^{02}k_H$ and only a quantitative comment is justified. The presence of methyl group in alanine may facilitate the transfer of electron from COOH in AH^- or COO^- group in A to the oxidant.

Activation parameters in the presence of SDS :

The activation energies of glycine and alanine in the presence of SDS are less than the activation energies observed in the absence of SDS. The slow reaction rates in the presence of SDS is probably due to the pre-exponential factor which is much less in the presence of SDS in comparison to pre-oxponential factor observed in the absence of SDS. On comparison of activation energies associated with reaction paths not affected by hydrogen ion ($^{-2}k_H$), it is obseved that the activation energy is much higher in the presence of surfactant in the case of glycine but it decrease significantly in case of oxidation of alanine. On the other hand, the reaction path adversely affected by hydrogen ion concentration has lower

TABLE-1 : KINETIC DATA FOR THE OXIDATION OF GLYCINE BY CHLORAMINE-T IN ACID MEDIUM

	Rate Constant Used	Thermodynamic Parameters*					Nature of rate constant
		Ea/kj mol^{-1}	ln A	$\Delta G^{\neq}$/kJ mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1}K^{-1}	
(a)	$^{02}k_G$	74.8	24.9	86.3	71.7	-48.5	$^{01}k_{obs}$ / [A]
	$^{-2}k_G$	66.8	21.3	87.0	64.3	-75.1	$^{-1}k_{obs}$ / [A]
	$^{+2}k_G$	74.8	25.3	85.3	71.7	-45.2	$^{+1}k_{obs}$ / [A]
(b)	$^{02}k_{HG}$	91.4	30.8	88.1	88.9	2.6	associated with reaction path unaffected by [H$^-$]
	$^{-2}k_{HG}$	149.6	52.5	91.6	147.1	183.1	
	$^{+2}k_{HG}$	41.6	11.4	87.1	39.1	-158.4	
	$^{01}k_{HG}$	49.9	11.6	94.9	47.4	-156.8	associated with reaction path adverse affect by [H$^-$]
	$^{-1}k_{HG}$	41.6	8.2	95.1	39.1	-184.8	
	$^{+1}k_{HG}$	91.4	28.1	94.8	88.9	-19.5	
	$^{-2}k_{mG}$	66.5	21.1	87.8	63.9	-78.5	associated with reaction in micellar phase
	$^{+2}k_{mG}$	8.3	1.1	79.8	6.2	-243.1	

*Thermodynamic parameters were determined in absence and presence of SDS and CPC in HCl medium at 303 K.

(a) $[H^+]$ = 0.05 mol dm^{-3}, (b) [Gly] = 0.03 mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}, [CPC] = 0.004 mol dm^{-3} and [CAT] = 2 x 10^{-3} mol dm^{-3}

TABLE-2 : KINETIC DATA FOR THE OXIDATION OF ALANINE BY CHLORAMINE-T IN ACID MEDIUM

	Rate Constant Used	Thermodynamic Parameters*					Nature of rate constant
		Ea/kj mol^{-1}	ln A	$\Delta G^{\neq}$/kJ mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1}K^{-1}	
(a)	$^{02}k_A$	58.2	19.0	84.5	55.7	-95.0	$^{01}k_{obs}$ / [A]
	$^{-2}k_A$	49.9	15.5	85.2	47.4	-124.7	$^{-1}k_{obs}$ / [A]
	$^{+2}k_A$	41.6	12.5	84.2	39.1	-148.8	$^{+1}k_{obs}$ / [A]
(b)	$^{02}k_{HA}$	97.7	33.8	88.9	97.2	27.4	associated with reaction path unaffected by [H$^-$]
	$^{-2}k_{HA}$	74.8	23.9	88.7	72.3	-54.1	
	$^{+2}k_{HA}$	49.8	14.7	86.9	47.3	-130.7	
	$^{01}k_{HA}$	24.9	2.7	92.5	22.4	-231.4	associated with reaction path adverse affect by [H$^-$]
	$^{-1}k_{HA}$	49.8	12.2	76.1	47.3	-95.1	
	$^{+1}k_{HA}$	41.5	9.4	92.2	38.9	-175.9	
	$^{-2}k_{mA}$	49.8	15.1	86.1	47.3	-128.1	associated with reaction in micellar phase
	$^{+2}k_{mA}$	20.7	5.4	81.5	18.2	-208.9	

*Thermodynamic parameters were determined in absence and presence of SDS and CPC in HCl medium at 303 K.

(a) $[H^+] = 0.05$ mol dm^{-3}, (b) [Ala] = 0.15 mol dm^{-3}, [SDS] = 0.01 mol dm^{-3}, [CPC] = 0.002 mol dm^{-3} and [CAT] = 2 x 10^{-3} mol dm^{-3}

activation energy for glycine as compared to activation energy in the absence of SDS. In case of alanine the trend is reversed that is activation energy in the presence of SDS is much higher as compared to the activation energy observed in the absence of SDS. It has been already pointed out that these rate constants are complex function of a number of equilibria involved in the reaction mechanism, therefore, a quantitative analysis of these parameters can not be made. The activation energy associated with the rate constant $^{-2}k_m$, representing reaction in the micellar phase is found to be similar to the activation energy for the oxidation in the aqueous phase in the case of glycine as well as for the oxidation of alanine as shown in (Table 1 and 2). In view of this, it appears that the inhibitory effect of negatively charged micelles on the reaction rate arises from steric and probability factors. It may be noted that pre-exponential factor in the absence of SDS is in the range of 10^{10} whereas in the presence of SDS it is in the range of 10^{8}.

Activation parameters in the presence of CPC :

In the presence of CPC the oxidation of glycine as well as alanine are significantly faster in comparison to the reaction in the absence of surfactant (Table 1 and 2). However, both the reactions show remarkably different characteristic of activation parameters in the case of glycine the overall activation energy associated with $^{+1}k_{obs}$ remains uncharged in comparison to the activation energy in the absence of any surfactant but the pre-exponential factor becomes increasingly higher with the concentration of CPC in comparison to on the other hand it is noted that

the pre-exponential factor in the presence of SDS with increasing concentration of SDS keeps decreasing wheras activation energy is only marginally affected. It appears that the oxidation of glycine the catalytic effect of CPC micelles and the inhibitory effect of SDS micelles are predominantly controlled by steric and probability factors represented by the pre-exponential factor. In case of alanine there is a 30% decrease in the activation energy with low pre-exponential factor. It appears that in this case the catalytic effect of CPC is exhibited largely due to lowering of activation energy. Comparison of activation parameters associated with the rate constant $^{+1}k_H$ representing reaction path adversely affected by hydrogen ion concentration shows the activation energy and pre-exponential remain uncharged. However, in case of the rate constant $^{+2}k_H$ representing the reaction path not affected by hydrogen ion concentration, the activation energy is only marginally affected but the pre-exponential factors increases 30 times in comparison to the pre-exponential factor observed in the absence of CPC. The fact that the catalytic effect of CPC micelles in the oxidation of alanine is dominated by activation energy variation is more clearly domonstrated when activation energy associated with rate constant $^{+2}k_H$ is examined.